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THE QUANTITATIVE DETERMINATION OF HALOGEN-ORGANIC COMPOUNDS OF THE ALIPHATIC SERIES

A. K. Ruzhentseva and V. V. Kolpakova

(The Serge Ordzhonikidze All-Union Scientific- Research Chemico-Pharmaceutical Institute, Moscow)

The most frequently used method for determining the halogen compounds of the aliphatic series is alkaline saponification. The respective inorganic halide thus formed is then determined by one of the usual methods.

The saponification reaction is not always quantitative and depends on many factors [1-5].

Experiments which we carried out on the saponification of different alkyl halides by means of 0.5 N alcoholic KOH in which the reaction mixture was heated on a water bath for 6-8 hours, confirmed that when these normal conditions of saponification are used, the reaction is not quantitative for many compounds. Some examples are given in Table 1.

TABLE 1

Saponification with 0.5 N alcoholic KOH for 6-8 hrs on a water bath[1)]

No.	Halide tested	g	Ml of 0.1 N $AgNO_3$ used	Halogen Found %	Halogen Computed %
1	Butyl chloride	0.1674 0.1461	8.28 6.23	17.54 15.27	38.35
2	Allyl bromide	0.2184 0.2240	16.00 16.42	58.55 58.58	66.12
3	Ethylene bromide	0.5140 0.6330	36.77 44.84	57.17 56.61	85.09

1) For other examples see V. S. Letina's work on "Methods for the quantitative determination of halogens in organic compounds by the action of the alkaline metals in an indifferent solvent". Moscow. All-Union Scientific- Research Chemico-Pharmaceutical Institute, (1947).

The use of high pressures (sealed tubes) in many cases leads to quantitative results. In this connection we carried out some experiments on the alkaline saponification of aliphatic halides in which an autoclave was used, in order to standardize the method of estimation. We used a rotating autoclave made of stainless steel with a capacity of 250 ml. In the first experiments the test

sample was placed in the autoclave with 0.5 N alcoholic KOH, the autoclave was set in motion and was heated externally by means of a burner. The internal temperature was held at 100° for 1 hour. The contents of the autoclave were then transferred into a conical flask and the halogen determined either by Volhard's method or potentiometrically.

For a number of halogen derivatives even these conditions were insufficient; the results obtained were low. Thus dichloroethane only gave 54.79% Cl; CCl_4 - 68.37%; and CH_2Cl_2 21.9%.

After further modifications of the temperature and the reaction medium we got results for different halides which agreed with theory. Saponification was carried out in the autoclave with a mixture of 0.5 N alcoholic KOH and 10% aqueous alkali for 1 hour at 200°. The results are given in Table 2.

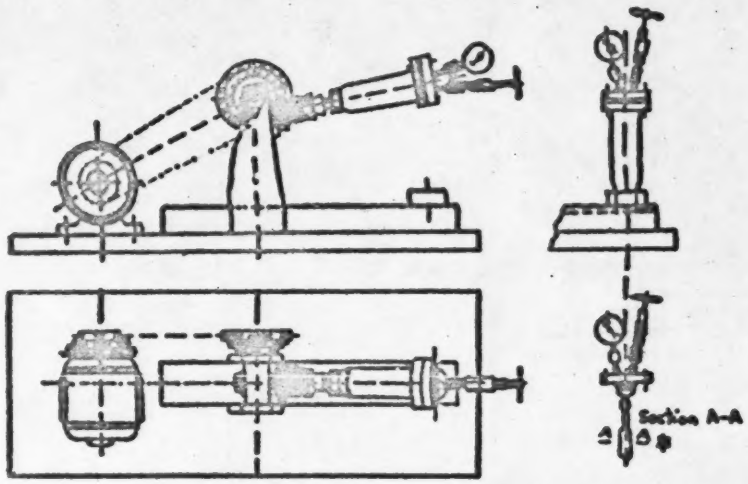
TABLE 2

No.	Compound analyzed	g	Ml of 0.1 N $AgNO_3$ used	Halogen Obtained %	Halogen Computed %	Recovery %
1	Butyl chloride	0.1286 0.1374	13.84 14.79	38.16 38.16	38.35	99.5
2	Methylene chloride . . .	0.1545	36.07	82.79	83.50	99.15
3	Dichloroethane	0.1778	35.57	70.94	71.67	98.99
4	Chloroform	0.1519	37.85	88.36	89.10	99.17
5	Carbon tetrachloride . .	0.1281	32.78	90.74	92.19	98.43
6	Hexachloroethane	0.1005	24.94	88.00	89.86	(Carius 87.98)
7	Ethylchloroformate . . .	0.2792	24.19	30.72	32.70	(Carius 30.69)
8	Dichloroacetic acid . .	0.1330 0.1383	20.46 21.28	54.55 54.56	55.01	99.1
9	Trichloroacetic acid . .	0.1281 0.1305	23.28 23.86	64.44 64.83	65.11	99.5
10	Chloretone	0.2020	32.36	56.81	56.47	100.60
11	Diethylaminoethylchloride	0.1617	11.90	26.10	26.1	100.0
12	Allyl bromide	0.1878 0.1608	15.54 13.29	66.13 66.11	66.12	100.0
13	Ethyl bromide	0.4800	48.50	72.43	73.3	98.81
14	Butyl bromide	0.4630 0.1701 0.1640	33.78 12.39 11.96	58.31 58.21 58.32	58.31	100.0
15	Ethylene bromide	0.1965 0.2504	20.93 26.73	85.13 85.31	85.09	100.04
16	Methyl iodide	0.3048 0.2600	21.50 18.36	89.52 89.62	89.43	100.10
17	Ethyl iodide	0.2524 0.2123	16.11 13.60	81.01 81.30	81.43	99.84
18	Iodoform	0.3182	24.28	96.84	96.69	100.15
19	Bromocamphor	0.2009	8.6	34.21	34.63	98.79

This table shows that recovery of the halogens under these conditions is complete and the method is of general application; (Cl, Br, I) are broken off from polyhalides and highly volatile compounds.

The method is very simple and only requires 2 hours for completion. In the course of the last 2 years we have used it for the determination of halogens in aliphatic compounds and have confirmed the results by means of the Carius method, with which we got good agreement.

The autoclave used is available; we got one from the Chemico-Analytical Laboratory of the Mendeleev All-Union Chemical Society (see diagram) but it can be made in any well equipped mechanical workshop.



Rotating autoclave

Description of the Method for the Determination of Halogens in Aliphatic Compounds

0.15–0.3 g (accurately weighed) of the test material is placed in a round thin-walled ampoule, the end of which is then sealed off. 20 ml of 0.5 N alcoholic KOH and 15 ml of 10% aqueous NaOH are placed in the autoclave. The end of the ampoule is broken off and placed together with it in the autoclave. The lid of the autoclave is hermetically sealed on and the apparatus set in rotation. It is heated externally for 1 hour. The temperature is maintained at ~200° (the thermometer is fixed in a case fitted to the autoclave). After cooling the excess pressure is released from the autoclave and the lid unscrewed. The contents are transferred quantitatively to a conical flask, and the halogens are then determined either by Volhard's method or potentiometrically.

If the test sample is solid, then it can be weighed in a boat; if it is a very volatile liquid, then the end of the glass ampoule should not be broken off before placing it in the autoclave, since it will be broken during rotation by the blades leading from the autoclave lid into the cup (the blades are made for the efficient stirring of the contents).

SUMMARY

A method is described for the quantitative determination of halogens in aliphatic halogen compounds (Cl, Br, I) by saponification with alcoholic-aqueous alkali in an autoclave maintained at 200° for 1 hour.

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THE QUANTITATIVE COLORIMETRIC DETERMINATION OF EPIHYDRIN ALDEHYDE FORMED DURING THE OXIDATION OF FATS

N. S. Drozdov and N. I. Materanskaya

Chair of Biochemistry, Moscow Chemico-Technological Institute of the Meat Industry

In the investigation of the oxidative break down of fats and fatty acids, the initial phase of this process which precedes the manifestation of organoleptic signs of break down is of particular importance. The determination of epihydrin aldehyde, which as we have shown in our own researches in particular, is one of the products characteristic of the first stages of oxidative changes in fat, is of vital importance in the methods employed for the study of the initial changes in fats which are subject to autoxidation.

Epihydrin aldehyde is determined in fats either qualitatively or in some instances approximately quantitatively by the development of a red color in the Kreis reaction [1].

Since Powick [2] and later Pritzker and Jungkunz [3] established that the reason for the development of a red color in the Kreis reaction for oxidized fats is the presence of epihydrin aldehyde in them, this reaction can be considered as specific for epihydrin aldehyde and consequently can be used for its quantitative determination. This characteristic of the Kreis reaction is not changed significantly, even if the opinion expressed in one of our investigations [4] is accepted, that in some instances the Kreis reaction is the result of, to some extent, the presence of higher homologs of epihydrin aldehyde in the oxidized fat.

Several investigations are noted in the literature in which attempts have been made to give a quantitative evaluation of the color which develops in the Kreis reaction, or to use this color for the quantitative determination of epihydrin aldehyde in fats. Holm and Greenbank [5] first proposed the use of acid solutions of methyred for approximate evaluation of the intensity of the color. Later a similar colorimetric method for the approximate evaluation of the intensity of the color developed in the Kreis reaction was described by Pritzker and Jungkunz [6] in which a solution of 1.2 mg of $KMnO_4$ in 100 ml H_2O was proposed as the solution for comparison. A more exact method of evaluating the intensity of the color of the reaction for ipihydrin aldehyde was the use of Lovibond red units, which was that adopted in Aas' method [7]. He established a linear relation between color intensity and the concentration of the colored reaction product.

A more detailed method for the determination of epihydrin aldehyde was studied by Taufel and Russow [8] who by means of epihydrin aldehyde which they synthesized, worked out a method for an approximate colorimetric determination with a standard color scale prepared from solutions of methyl red and permanganate. In a later publication Taufel and Seuss [9] proposed a scale which approximates closely to the colors of the Kreis reaction. This scale was prepared by the dilution of a 0.1% aqueous solution of acid fuchsin with acidified water.

All the methods which have been mentioned only given an approximately quantitative expression for the determination of epihydrin aldehyde. Only in Pyke's [10] work was the relation between the color intensity as measured by means of red Lovibond filters, and the concentration of epihydrin aldehyde investigated. This was expressed by the formula

$$\text{Red Lovibond units} = 97\ (C_3H_4O_2\%) + 0.625$$

and in this way indicated a more accurate method for the colorimetric determination of epihydrin aldehyde.

It should be noted, that different methods of carrying out the Kreis reaction itself are given in all the references cited. This can be explained by the difficulties which arise in attempting to use the color of a reaction for quantitative and semiquantitative determinations, and is connected with the choice of color scale and choice of method for carrying out the colorimetric determination, and also with the method of realizing the Kreis reaction itself. The intensity of the color in the Kreis reaction depends not only on the quality, and ratios of the reactants in the reaction mixture, but also on the temperature and reaction time.

In addition, in some instances when the color reaction is carried out, fine emulsions or supplementary colors can be formed in the colored layer, the presence of which interferes with exact colorimetric determination. This fact compelled Tauffel and Seuss in the work already cited, instead of carrying out the usual method for the reaction, to use a preliminary distillation of the epihydrin aldehyde in a stream of air; the distilled aldehyde was then trapped in a mixture of equal parts of 1% solution of phloroglucinol in alcohol, and concentrated sulfuric acid. In order to accomplish this a special apparatus described by Tauffel and Sadler [11] is necessary. In addition a number of precautions must be taken, which nevertheless do not guarantee freedom from errors connected with possible losses of epihydrin aldehyde as a result of incomplete absorption, or further oxidation by atmospheric oxygen. All these drawbacks deprive the roundabout distillation method of any advantages it has over the usual method of carrying out the reaction.

In an attempt to work out a method for the determination of epihydrin aldehyde which is not only reliable enough but is also simple and can be carried out in any laboratory, we left out the distillation method which is lengthy and unreliable and necessitates the use of special apparatus, and instead concentrated on the usual technique for carrying out the color reaction. Such a method in which certain conditions are observed, at least for the vast majority of fats and fatty acids, does not lead to any appreciable deviations in the intensity of the color developed, which might affect the results. We established that if a solution of 1 ml of the test fat in 2 ml of ether is mixed with 1 ml 37% chemically pure HCl, and shaken up, followed by the addition of 2 ml of a 0.1% solution of phloroglucinol in ether, and the final mixture again shaken and heated for 1 minute at 100°, a color develops in the lower aqueous layer the volume of which is 2 ml. This color attains a maximum in 1 minute, after which it remains fairly constant for some time, and then begins to weaken or changes its character. Thus a colorimetric determination can be carried out under these conditions 2 minutes after mixing the reagents.

Further, in contrast to Pyke we found that the relation between color intensity as measured by Lovibond red units and the concentration of epihydrin aldehyde solutions was expressed more closely by the formula:

$$\text{Red Lovibond units} = 100\ (C_3H_4O_2\%) + 0.60.$$

In order to simplify as much as possible the colorimetric part of the determination, we made up a series of standard colored liquids. Colorimetric determination is thus carried out by simple comparison by means of a comparator of the colors developed in the Kreis reaction with standard colors. We used acid fuchsin for the preparation of these standards, since acid fuchsin solutions are the only ones of all the colored solutions proposed for this purpose, which have colors practically identical with that developed in the epihydrin aldehyde reaction. The preparation of a color scale is very simple and is accomplished by dilution to a range of concentrations of a stock 1% aqueous solution of acid fuchsin with distilled water, 1000 ml of which contains approximately 0.5 ml 20% sulfuric acid. The colors of the solutions obtained are sufficiently stable if they are kept in sealed or well stoppered test tubes. The intensity of the colors hardly changes at all in the course of four months if protected from the action of direct or very intense diffuse solar light.

The volumes of a 0.1% solution of fuchsin in ml necessary to prepare standard solutions by making up to a volume of 50 ml with water are given in the table below. In addition, the intensities of the colors measured in red Lovibond units and the corresponding concentrations of epihydrin aldehyde are included.

No.	Vols. of 0.1% fuchsin solution in ml to be made up to 50 ml with acidified water	Color intensity (Red Lovibond units)	Mg of epihydrin aldehyde in 1 ml of liquid
1	0.05	0.75	0.015
2	0.1	1.5	0.090
3	0.2	3.0	0.240
4	0.3	4.5	0.390
5	0.4	6.0	0.540
6	0.5	7.5	0.690
7	0.6	9.0	0.840
8	0.7	10.5	0.990
9	0.8	12.0	1.140
10	0.9	13.0	1.240

Such a scale is sufficiently accurate for normal practical determination of epihydrin aldehyde. If it is required to increase the accuracy, intermediate standards can be prepared at different parts of the scale, so that the scale can be supplemented with standard solutions, for which, by simple interpolation it is easy to find the value of the corresponding concentration of epihydrin aldehyde. It should be remembered that the accuracy of the determination depends on a number of factors; the accuracy of the measurement of the volume of the liquid being colorimetrically determined, the stability of the reaction colors, the influence of temperature and other factors.

The method adopted was briefly as follows:

An accurately weighed aliquot of $\sim$1 g of the test fat or fatty acid is placed in a graduated flask of colorless glass fitted with a ground glass stopper of the same size as the flask, and dissolved in 2 ml of ether. 1 ml of 37% chemically pure HCl is added and the mixture shaken. 2 ml of a 0.1% solution of phloroglucinol in ether is then added and the whole shaken again after which it is

placed on a boiling water bath for 1 minute. The test tube is withdrawn from the bath and after 1 minute the color of the lower layer is compared with the standards in a comparator. The determination should occupy in all only 10 minutes. The volume of colored layer is measured, and from the value found for the concentration of epihydrin aldehyde and the volume of the colored liquid the content of epihydrin aldehyde in the aliquot taken, or in 100 g of the test fat, is calculated.

The color reaction with phloroglucinol is very sensitive; by means of it 0.0005 mg of epihydrin aldehyde in 1 ml can be detected. If resorcinol or naphthoresorcinol are substituted for phloroglucinol the sensitivity decreases. Thus, when resorcinol is used, the limiting concentration of aldehyde which can be detected by the development of a color is 0.01 mg/ml.

The method described for the determination of epihydrin aldehyde gives good concurrent results for the majority of fats and fatty acids which are in the initial stages of autoxidation. The method however is not applicable to fats which have an intense inherent color, or to fats and fatty acids containing additives which give colors with the reagents used in the colorimetric determination, or for cases of strongly oxidized fats for which the content of epihydrin aldehyde is not a true indication of the break down.

SUMMARY

A simple method is described for the quantitative colorimetric determination of epihydrin aldehyde formed during the oxidation of fats and fatty acids. The method is based on the formation of colors in the Kreis reaction. The method described can be used in any laboratory and enables the determination to be carried out in 10 minutes with an accuracy which is satisfactory for most practical purposes.

The factors which affect the results are pointed out, as well as the cases in which the colorimetric method described is inapplicable.

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THE QUANTITATIVE DETERMINATION OF THE DEHYDRATION OF CERTAIN ALCOHOLS

N. Z. Kotelkov and K. P. Kotelkova

(Saratov Agricultural Institute)

It has been established [1,2,3] that the process of catalytic dehydration of certain alcohols followsa well defined path, i.e. water and the corresponding hydrocarbon are formed.

When it is necessary to control the reaction, particularly if dehydration is being studied in a stream of gas, it is very important to follow the path of the process not only by the amount of gas formed, but also by the amount of water formed. The latter can easily be tracked if the original material is mixed with water in any ratio, and the binary aqueous-alcohol mixture possesses some property which is simply related to the quantitative ratios of the components. We have shown in our investigations that the refractive index is such a property for ethyl and propyl alcohols, this being especially true for mixtures containing 40-60 mol% water and more.

In a simple process the degree of dehydration is linearly dependent on the gas which is formed, while the relation between dehydration and the refractive index is more complex; the refractive index n of a two component mixture is related to the density d which is variable, by one of the following relations

$$\frac{n-1}{d} = \text{const}, \quad \frac{n^2-1}{d} = \text{const} \quad \text{and} \quad \frac{1}{d}\,\frac{n^2-1}{n^2+2} = \text{const}$$

which can afterwards be related to the refractive indices of the components and their content in percentage weight. More details are given in the works of Pavlov [4], Doroshevsky [5], and others. Nevertheless, the practical application of the relations given above is complicated, as a result of the introduction of correction factors and the complexity of the calculations.

The aim of this present work, while not dwelling on the theory of this important and interesting question, is to give a possible quantitative method for the determination of dehydration by means of the refractive index on the basis of the tables given below, which were compiled from the results of careful measurements.

As investigations [5,6] have shown, aqueous solutions of the alcohols examined have a maximum for the refractive index, which is observed at 15-25° in mixtures containing 16-20 wt % or 33-39 mol % of water; 5-6 wt % or 16-18 mol % ethyl alcohol; and 3 wt % or 10 mol % of isopropyl alcohol. According to our work (vide tables) the maximum in solutions of ethyl and n-propyl alcohol is approximately the same; while in the isopropyl alcohol the maximum is at 8 mol %.

The accuracy of the results determined by refractive index depends not only on the accuracy of the refractometer itself, but also on the degree of dehydration. For the Abbe refractometer which we used the following accuracies were obtained 1) in the case of ethyl alcohol for 58% dehydration the error does not exceed 0.73%; for 63%-0.47%; for 72% - 0.26%; for 80% - 0.17%; for 85% - 0.1% and for 90% and over not more than 0.07-0.05%.

2) In the case of n-propyl alcohol, for 40% dehydration the error is equal to 0.62%; for 51% - 0.42%; for 65.5% - 0.31%; for 76.6% - 0.11%; over 76.6% - 0.03%.

3) In the case of isopropyl alcohol for 50% dehydration the error is equal to 0.63%; for 60% - 0.31%; for 8' % - 0.1%; over 84% down to 0.02%.

Obviously with increasing dehydration the accuracy of determination increases and the error decreases for the propyl alcohols 0.03-0.02%.

The accuracy of the results calculated from the gas depends on the accuracy of the measurement of t°, P and V. If inaccuracies in the measurements of t° and P are neglected, and the volume of gas is measured with an accuracy of 0.5 ml/500 ml, the error in any result will be 0.1%, and only when the volume can be measured with an accuracy of 0.1 ml will the error fall to 0.02%.

Consequently the refractive index method can be successfully used for the quantitative determination of dehydration when the degree of dehydration of the particular alcohol concerned is greater than 50-60%.

Original Materials

The water was twice distilled and its refractive index determined. Doroshevsky's results and others from the Technical Encyclopedia are given for comparison.

	Doroshevsky	Tech.Encyc. Vol.VIII p.42	Our Results
n_D^{15}	1.33339	1.3334	1.3334
n_D^{20}	1.33298	1.3330	1.3330
n_D^{25}	1.33258(n_D^{24})	1.3325	1.3325
d_4^{20}	0.99823		

The alcohols were also twice distilled and the middle fractions taken. They were dehydrated by Doroshevsky's method. His results and those from the Technical Encyclopedia are included for comparison:

1. Ethyl Alcohol

Chemical Handbook, 19-8	Tech. Encyl. Vol.V p.159	Doroshevsky
d_4^{20} 0.789	0.78934	0.7886 (22°)
d_4^{25} -	0.78506	0.7851

Our Results	Tech. Encyl. Vol.VIII p.79, 45	Doroshevsky
n_D^{15} -	1.36332	1.36230 (17.5°)
n_D^{20} 1.3614	1.36242 (18.35°)	1.36127
n_D^{25} 1.3593	-	1.3594

3. Isopropyl Alcohol

Chemical Handbook 1[illegible]	Tech. Encyl. p 46	Doroshevsky p.130 (Bryul)
d_4^{20} 0.785	0.7887	0.7887

Our Results	Tech. Encyl.	Doroshevsky p. 251
n_D^{15} 1.3793	1.3792	1.37922
n_D^{20} 1.3774	1.37757	1.37727
n_D^{25} 1.3755	-	-

2. n-Propyl Alcohol

	Chemical Handbook	Tech. Encycl. Vol. VIII p. 46	Doroshevsky p. 123
d_4^{20}	0.803	0.8044	0.80365

	Our Results	Tech. Encycl. p. 46, 92	Doroshevsky
n_D^{13}	1.3873	1.38726	1.38729
n_D^{20}	1.3854	1.38543	1.38547

TABLE 1

Dehydration of Ethyl Alcohol According to Refractive Index

No.	Water, wt. %	% Dehydration	n_D^{20}	n_D^{23}	n_D^{25}	$\frac{\Delta n}{\Delta t} \cdot 10^4$
1	Pure Ethyl alcohol	-	1.3614	1.3601	1.3593	4.2
2	0.92	2.32	19	06	98	4.2
3	3.02	7.37	26	13	1.3605	4.2
4	5.27	12.45	32	20	11	4.2
5	8.28	18.76	39	26	18	4.2
6	11.36	24.68	44	32	23	4.2
7	14.95	31.01	47	35	27	4.0
8	20.00	39.00	49	37	29	4.0
9	25.01	46.03	48	36	28	4.0
10	30.04	52.34	45	33	25	4.0
11	35.04	57.97	40	28	20	4.0
12	40.05	63.07	33	21	13	4.0
13	45.07	67.72	23	12	04	3.8
14	50.00	71.89	12	02	1.3595	3.4
15	51.65	73.20	07	1.3597	90	3.4
16	54.07	75.07	00	91	84	3.2
17	55.33	76.00	1.3596	87	80	3.2
18	57.18	77.35	89	80	74	3.0
19	60.65	79.76	78	69	63	3.0
20	61.67	80.45	74	65	59	3.0
21	62.82	81.20	68	59	53	3.0
22	64.39	82.22	61	52	46	3.0
23	65.64	83.01	56	47	41	3.0
24	66.37	83.46	53	44	38	3.0
25	67.29	84.03	48	40	34	2.8
26	68.47	84.74	1.3542	1.3534	1.3528	2.8
27	68.87	84.98	40	32	26	2.8
28	69.75	85.50	35	27	22	2.6
29	70.78	86.11	29	21	16	2.6
30	73.30	87.56	14	07	02	2.4
31	74.76	88.34	06	1.3499	1.3495	2.2
32	77.83	89.97	1.3485	79	75	2.0

(Continued on next page)

Table 1 (continued)

No.	Water, wt. %	% Dehydration	n_D^{20}	n_D^{23}	n_D^{25}	$\frac{\Delta n}{\Delta t} \cdot 10^4$
33	79.46	90.82	73	68	64	1.8
34	82.96	92.57	48	43	40	1.6
35	86.00	94.02	25	21	18	1.4
36	87.56	94.74	13	09	06	1.4
37	90.00	95.84	1.3395	1.3391	1.3388	1.4
38	90.73	96.16	90	86	84	1.2
39	91.65	96.56	83	79	77	1.2
40	93.65	97.24	72	68	66	1.2
41	95.20	98.07	60	56	54	1.2
42	95.77	98.31	57	54	52	1.0
43	97.08	98.84	49	46	44	1.0
44	98.45	99.39	41	38	36	1.0
45	98.63	99.46	40	37	35	1.0
46	98.98	99.58	38	35	33	1.0
47	99.24	99.70	36	33	31	1.0
48	99.37	99.81	34	31	29	1.0
49	99.87	99.95	31	28	26	1.0
50	100	100	30	27	25	1.0

TABLE 2

Dehydration of n-Propyl Alcohol according to Refractive Index

No.	Water, wt. %	% Dehydration	n_D^{15}	n_D^{20}	$\frac{\Delta n}{\Delta t} \cdot 10^4$
1	Pure Propyl alcohol	-	1.3873	1.3854	3.8
2	0.62	2.04	73	55	3.6
3	1.6	5.14	73	55	3.6
4	2.3	7.28	74	55	3.8
5	3.6	11.08	74	55	3.8
6	5.2	15.47	71	53	3.6
7	6.66	19.23	65	47	3.6
8	8.7	24.12	60	42	3.6
9	10.0	27.04	57	39	3.6
10	10.8	28.77	55	37	3.6
11	12.12	31.52	52	34	3.6
12	13.59	34.41	48	30	3.6
13	16.63	39.96	40	22	3.6
14	20.0	45.47	32	14	3.6
15	21.59	47.93	28	10	3.6
16	23.00	49.91	24	06	3.6
17	23.71	50.90	22	04	3.6
18	26.20	54.22	14	1.3796	3.6
19	28.80	57.43	1.3805	88	3.4
20	30.00	58.84	07	84	3.4
21	32.40	61.52	1.3793	76	3.4
22	34.77	64.00	85	68	3.4
23	37.0	66.21	77	60	3.4
24	38.38	67.51	72	55	3.4
25	40.00	68.99	66	50	3.2

Table 2 (continued)

No.	Water, wt. %	% Dehydration	n_D^{15}	n_D^{23}	$\frac{\Delta n}{\Delta t} \cdot 10^4$
26	42.27	70.93	56	40	3.2
27	45.22	73.36	39	23	3.2
28	47.40	75.04	26	10	3.2
29	49.54	76.61	13	1.3698	3.0
30	50.00	76.94	1.3710	1.3695	3.0
31	53.00	79.00	1.3692	77	3.0
32	55.28	80.48	78	64	2.8
33	57.01	81.56	69	55	2.8
34	60.00	83.35	53	40	2.6
35	62.3	84.64	40	27	2.6
36	65.29	86.25	22	09	2.6
37	65.9	86.57	19	06	2.6
38	67.95	87.61	06	1.3594	2.4
39	70.00	88.62	1.3592	80	2.4
40	71.28	89.22	84	72	2.4
41	73.56	90.27	70	58	2.4
42	74.51	90.70	63	52	2.2
43	76.8	91.70	49	38	2.2
44	78.9	92.58	34	24	2.0
45	80.0	93.03	23	14	1.8
46	83.54	94.41	1.3492	1.3484	1.6
47	86.9	95.68	61	54	1.4
48	90	96.78	31	25	1.2
49	90.28	96.87	28	22	1.2
50	91.73	97.37	13	08	1.0
51	95.70	98.67	1.3374	1.3369	1.0
52	97.12	99.12	61	57	0.8
53	97.71	99.30	55	51	0.8
54	98.10	99.42	52	48	0.8
55	98.45	99.53	49	45	0.8
56	98.81	99.64	46	42	0.8
57	99.14	99.74	43	39	0.8
58	99.43	99.83	40	36	0.8
59	99.73	99.92	37	33	0.8
60	100	100	34	30	0.8

TABLE 3

Dehydration of Isopropyl Alcohol According to Refractive Index

No.	Water, wt. %	% Dehydration	n_D^{20}	n_D^{23}	n_D^{25}	$\frac{\Delta n}{\Delta t} \cdot 10^4$
1	Pure Isopropyl alcohol	-	1.3774	1.3763	1.3755	3.8
2	2.51	7.91	76	64	56	4.0
3	3.29	10.19	74	62	54	4.0
4	7.09	20.29	71	58	50	4.2
5	11.57	30.38	68	57	49	3.8
6	16.91	40.43	61	50	42	3.8
7	19.98	45.44	57	46	38	3.8
8	23.39	50.45	51	40	32	3.8
9	27.17	55.44	43	32	25	3.6

Table 3 (continued)

No.	Water, wt. %	% Dehydration	n_D^{20}	n_D^{23}	n_D^{25}	$\frac{\Delta n}{\Delta t} \cdot 10^4$
10	31.41	60.43	32	21	14	3.6
11	33.75	62.95	26	15	08	3.6
12	36.17	65.40	18	07	00	3.6
13	38.82	67.91	09	1.3699	1.3691	3.6
14	41.59	70.37	1.3699	89	82	3.4
15	43.05	71.60	94	84	77	3.4
16	44.58	72.85	88	78	71	3.4
17	46.17	74.10	82	72	65	3.4
18	47.79	75.33	76	66	60	3.2
19	49.50	76.58	70	60	54	3.2
20	51.25	77.81	63	54	48	3.0
21	53.08	79.05	56	47	41	3.0
22	54.96	80.28	49	40	34	3.0
23	56.96	81.53	41	32	26	3.0
24	59.00	82.76	32	23	17	3.0
25	61.15	84.00	1.3622	1.3614	1.3608	2.8
26	63.37	85.23	10	02	1.3597	2.6
27	65.71	86.47	1.3597	1.3589	84	2.6
28	68.11	87.69	82	75	70	2.4
29	70.66	88.93	67	60	56	2.2
30	73.31	90.16	50	44	40	2.0
31	75.54	91.15	35	30	26	1.8
32	77.82	92.13	19	14	11	1.6
33	80.23	93.12	1.3492	1.3497	1.3494	1.6
34	82.70	94.10	84	80	77	1.4
35	85.31	95.09	64	60	57	1.4
36	89.99	96.07	42	38	36	1.2
37	90.82	97.06	18	14	12	1.2
38	92.27	97.55	06	02	00	1.2
39	93.75	98.04	1.3392	1.3388	1.3386	1.2
40	95.26	98.53	79	75	73	1.2
41	96.83	99.02	63	60	58	1.0
42	97.19	99.14	60	57	55	1.0
43	97.74	99.31	55	52	50	1.0
44	98.38	99.51	48	45	43	1.0
45	99.68	99.60	45	42	40	1.0
46	99.14	99.74	41	38	36	1.0
47	99.47	99.84	37	34	32	1.0
48	100	100	30	27	25	1.0

EXPERIMENTAL

The water-alcohol mixtures were prepared by volume and by weight in special flasks fitted with ground glass stoppers with capacities of 12-20 ml for solutions containing water up to 99 mol.% and in 50 ml flasks for more dilute solutions. The solutions were made up a few times and the determinations of the refractive index were also repeated as a check. The temperature of the apparatus was maintained at the necessary level and the refractometer prism washed with water at the same temperature.

The refractive index was determined at 20, 23 and 25° for ethyl alcohol-

water and isopropyl alcohol-water and at 15 and 20° for n-propyl alcohol-water mixtures.

The $\frac{\Delta n}{\Delta t} \cdot 10^4$ column in the tables shows the change of refractive index with a change of 1° in temperature. The results are given in Tables 1, 2 and 3. When no value is given in the table for the refractive index, the percentage dehydration is calculated by interpolation, on the assumption that for small intervals the relationship is linear.

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SUMMARY

1. The relation between percentage composition and the refractive index of binary aqueous-alcohol mixtures has been studied.

2. A refractive index method can be successfully applied to the quantitative determination of the dehydration of certain alcohols, particularly when dehydration is more than 40-60%.

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SPECIFIC REACTIONS AND METHODS IN ORGANIC ANALYSIS

1. THE DETECTION AND QUANTITATIVE DETERMINATION OF TRACES OF PIPERIDINE IN THE PRESENCE OF PYRIDINE

L. M. Kulberg and I. S. Mustafin

(The Chernyshevsky Saratov State University)

In recent years a number of more or less successful attempts have been made to apply specific reactions to the analysis of organic compounds. It is obvious that the solution of this question in the contemporary chemistry of organic compounds is of paramount scientific and practical importance; at the same time, the investigator is faced with difficulties, to surmount which is far beyond the limits of possibility for the majority of the corresponding classical methods.

At the present time it is impossible to point out any general approach for the solution of each concrete problem within the present framework of ideas. One of us has shown that in a number of instances good results can be obtained by changing the substance sought and which is present in a mixture with other substances of similar structure, into the corresponding specific reagent, which in turn can be detected by means of a suitable inorganic compound [1].

Naturally this method is not the only possible one; for the solution of the problems indicated, other methods from the arsenal of organic and analytical methods can be applied. In particular, we are convinced that the application of specific complex formation, and the use of reactions as a result of which molecular compounds of the substances sought are formed with inorganic or organic components, will lead to a successful solution.

A multitude of more or less specific reactions for whole classes of compounds possessing functional groups are known in the contemporary chemical analysis of organic compounds; unfortunately these reactions are far from universal, and particularly serious difficulties are encountered when complex multifunctional individuals are dealt with. In addition, the abundance of different organic compounds frequently of similar properties (derivatives of penta and hexa-methylene, pyridine and piperidine etc.), sometimes even belonging to different classes (derivatives of benzene and thiophene, pyrrole, furane, etc.) makes it an essential problem to develop reactions which are not universally specific for a whole class (there are actually no such reactions in organic chemistry), but exhibit a strictly intraclass specificity. Such an approach in the chemical analysis of organic compounds, in the opinion of the authors, has great practical significance.

The present article is devoted to the detection and quantitative determination of piperidine in the presence of pyridine.

While there is a number of characteristic color reactions for pyridine by means of which it can be detected in the presence of piperidine, the solution of the reverse problem (piperidine in the presence of pyridine) is extremely difficult. We could only find one reaction for piperidine in the literature and that was of low specificity – the use of acetaldehyde and sodium nitroprusside [2]. With respect to the quantitative determination of piperidine in the presence

of pyridine, as far as we know[1] only one method, a straight potentiometric method has been described [3]. This method naturally cannot be applied even when the amount of piperidine to pyridine approximates to 1-5%.

Thus, in fact up to the present time there has been no method available for the qualitative detection and quantitative determination of traces of piperidine in the presence of pyridine. Meanwhile the necessity for suitable methods and their scientific and practical importance can scarcely be disputed.

Diltey and Witzingen [4] as long ago as 1926 made a curious observation, re the formation of colorless complex compounds between certain triphenylmethane dyes and piperidine, in contrast to pyridine which does not yield complexes. These observations were confirmed in a further series of investigations by Rumanian workers [5,6] who also established that ammonia behaves in a similar fashion to piperidine. Our work, shows that in addition to piperidine and ammonia, colorless compounds are also formed as the result of interaction between these triphenylmethane dyes and ethylenediamine, and monoethanolamine. Further, we established that a number of other amines and in general organic bases, particularly diisoamylamine, diisobutylamine, isobutylamine, lutidine, isobutylidene, tetramethylpyridine, trimethylpyridine, diethanolamine, triethanolamine, triethanolamine triacetate, monoethanolamine diacetate, and the N-mono acetate of monoethanolamine do not react with these triphenylmethane dyes under similar conditions.

These facts gave grounds for assuming that the interaction of piperidine (PPR) with triphenylmethane dyes proceeds according to the scheme

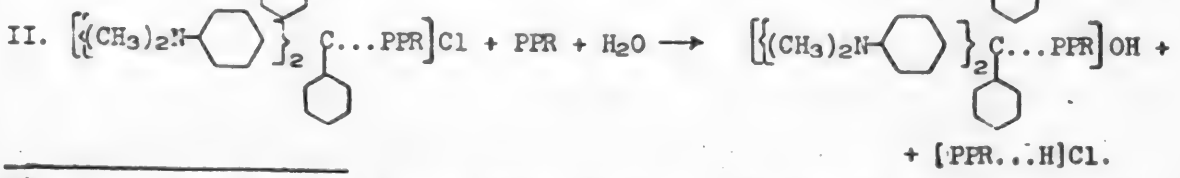
$$\underset{\text{colored}}{[Ar_3C]X} \underset{\text{water}}{\overset{\text{piperidine}}{\rightleftharpoons}} \underset{\text{colorless}}{[Ar_3C\ldots PPR]X}$$

and that the decolorization which accompanies the reaction can be used as the basis for a specific method for the detection and determination of piperidine in the presence of pyridine and its homologs. The interfering action of ammonia, the presenceof which in technical products is not excluded, can be eliminated by known methods.

Triphenylmethane dyes such as crystal violet and fuchsine, form complexes with piperidine which are easily decomposed by water. Water acts similarily with the reaction products of these dyes with ammonia. Malachite green on the other hand reacts with piperidine (but not ammonia) to form a complex compound of the carbinol base type which is stable to water. This fact makes malachite green particularly suitable as a reagent for piperidine (PPR).

Thus as a basis for our proposed method for the detection and quantitative determination of piperidine in the presence of pyridine we have the following reactions

I.

II. 

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[1] In addition there is a brief description of a method for the quantitative determination of piperidine in the presence of pyridine, by converting it into the corresponding dithiocarbonate [7].

The effect of the reaction is decolorization of the malachite green. It should be noted that the proposed method could be successfully used for the detection and determination of monoethanolamine in the presence of its homologs and derivatives, and also of ethylenediamine in the presence of aliphatic amines. The qualitative reaction for piperidine with malachite green is carried out by spot test technique on reagent paper soaked with a solution of the dye. When a drop of pyridine containing piperidine is placed on the reagent paper, formation of a colorless spot occurs in a few seconds or if the concentration of piperidine is low, partial decolorization can be observed. The stability of the spot in air depends on the concentration of piperidine in the test solution. Thus, e.g. for a concentration of 0.1% of piperidine in pyridine, decolorization of the spot can be observed and the white color is completely stable; for piperidine concentrations less than 0.1%, only partial decolorization is observed as compared with a control spot, prepared by the use of piperidine-free pyridine. In this way it is possible to detect piperidine in concentrations not less than 0.05%. Spots, however which have been formed by pyridine solutions of piperidine in concentration of from 0.05 - 0.1% regain a green color on standing for some time.

It is possible therefore to detect 1 μg of piperidine, for a limiting ratio of piperidine to pyridine of 1:2000 (0.05% solution).

The quantitative determination of the piperidine is based on the measurement of the decrease in the light absorption coefficient of the malachite green solution as a result of the effect of test solutions.

As can be seen from Fig. 1 the maximum absorption of a methanol-pyridine solution of malachite green lies near 610 mμ. Consequently, colorimetric measurements must in this case be made in the spectral region, corresponding to the indicated wave length.

A calibration curve is given in Fig. 2 and it follows from this that the weakening of the color of the reagent solution when acted upon by the test solutions does not obey the Lambert Beer law.

Results are given in the table which characterize the accuracy of the results obtained on the determination of piperidine in pyridine.

It is clear from the table that it is possible to determine piperidine in pyridine at concentrations of 0.01% and higher with a fair degree of accuracy, by means of the method proposed.

Quantitative Determination of Piperidine in Pyridine by Means of Malachite Green

Content of piperidine in pyridine (%)	Piperidine taken, μg	Piperidine found, μg	Error in μg	Error in %
0.010	100	100	0	0.0
0.012	115	120	+5	-4.3
0.013	125	120	-5	4.0
0.014	135	135	0	0.0
0.015	150	150	0	0.0
0.017	175	175	0	0.0
0.020	200	207	+7	3.5
0.021	210	208	-2	0.9
0.023	225	225	0	0.0
0.025	250	250	0	0.0

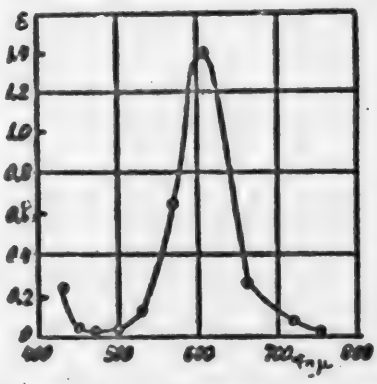

Fig. 1. Light absorption curve for a methanol-pyridine solution of malachite green.

EXPERIMENTAL

Reagent. The reagent used was a 0.1% solution of the pure dye, malachite green (for bacteriological purposes) in colorless, freshly distilled anhydrous pyridine. The dye dissolves on warming slightly; the solution thus obtained is colored a blue-green which quickly turns pale.

Reagent paper is prepared by soaking strips of filter paper in the reagent solution and drying at 60-70°. Where the reagent paper is to be used for detecting less than 0.1% piperidine, it is necessary to use a reagent solution of 0.05% malachite green (prepared by diluting the base solution of the dye twice) for soaking the strips. Both the reagent solution and paper are stable

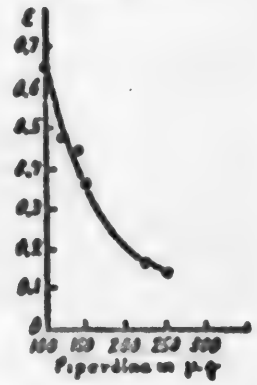

Fig. 2. Calibration curve for spectrophotometric determination of traces of piperidine in pyridine.

Detection of Piperidine in Pyridine. A drop of the pyridine which is to be tested for piperidine is placed on the reagent paper by means of a capillary. If more than 0.1% of piperidine is present in the pyridine a stable white spot appears on the green background of the paper after a few seconds. For concentrations of piperidine less than 0.1%, complete decolorization is not observed, instead only a weakening of the color at the point where a drop of test solution was placed, occurs. This weakening of the color is compared with a spot obtained by the use of a drop of pyridine free from piperidine on the filter paper.

If the decolorization or weakening of the color is the result of the action of ammonia and not piperidine, the spot is unstable and its color soon becomes comparable with the general background.

The Quantitative Determination of Piperidine in Pyridine. To 1 ml of the pyridine to be tested contained in a test tube are added 0.5 ml of the 0.1% reagent solution of malachite green and 2.5 ml of pure methyl alcohol; the test tube is thoroughly shaken and placed on a water bath at 60-70° for 1-2 minutes.

The contents of the test tube after cooling are transferred to the cell of a photometer of the Pulfrich type with d = 5 mm and colorimetrically determined with a light filter S = 61; water is used as the condensing liquid. Calculations are made on the basis of a calibration curve prepared beforehand (Fig. 2).

We recommend that each investigator should prepare his own calibration curve for any given sample of malachite green. In addition it should be born in mind that high values for light absorption correspond to low concentrations of piperidine.

SUMMARY

1. A method is proposed for the qualitative (spot test) detection and quantitative (colorimetric) determination of traces of piperidine in pyridine.

2. The method is based on the formation of a complex compound between piperidine and malachite green.

3. By means of this method 1 μg of piperidine can be detected in pyridine for a ratio of piperidine to pyridine of 1:2000; it is possible to determine quantitatively amounts of 0.01% and over of piperidine in pyridine.

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A COLOR REACTION FOR DICHLOROETHANE

V. I. Kuznetsov and Z. M. Pimenova

(The Sanitary-Epidemological Station, Kirov region, Moscow)

1,2-Dichloroethane CH_2ClCH_2Cl (b.p. 83.5°) which is easily available finds considerable application as a volatile solvent for the extraction of fats and fatty substances, and in the preparation of various lakes, etc. [1].

Dichloroethane is toxic. The tolerance limit for it in the atmosphere of places of work is 0.05 mg/l [2]. In this connection, it is often necessary to detect the presence of dichloroethane either in the air, or as a component of mixed solvents. Existing methods for the detection and determination of dichloroethane are based on saponification or on combustion to HCl. The Cl ion is then determined nephelometrically with $AgNO_3$ [3,4,5]. It is obvious that all halogen containing compounds will thus be determined as dichloroethane.

We have been unable to find in the literature descriptions of any specific reaction for dichloroethane, which would enable it to be determined in the presence of other solvents. In the present article, a new color reaction which is specific for dichloroethane is described, and which is based on the formation of a red color on heating quinoline and dichloroethane.

Procedure

0.2-0.3 ml of quinoline which is not too dark or, better still, which is freshly redistilled (b.p. 238°) is placed in a test tube and one drop of dichloroethane, or the solvent suspected of containing dichloroethane added. The test tube is placed in a glycerine bath heated to 200° and left in it for 3-4 min. It is better to heat on an electric hot plate or on a gas burner. In the presence of a large amount of dichloroethane the quinoline on slow, prolonged, heating develops a brown or brownish-red color; on heating it quickly the color attained is a bluish-red color. For small amounts of dichloroethane the color of the quinoline becomes orange-yellow. In the absence of dichloroethane no color develops.

Dilution of the quinoline with indifferent solvents which boil below 200°, impairs the reaction, since the reaction has an optimum rate at 190-200°. The quinoline can be diluted two or three times with non-aqueous, colorless glycerine or naphthalene without significantly impairing the clarity of the reaction.

This reaction can be used for the detection of 5-10% of 1,2-dichloroethane in chloroform, xylene, carbon tetrachloride, chlorobenzene, 1,1-dichloroethane (ethylene chloride), and in a number of other solvents. If the content of dichloroethane is less than 5%, then it will be necessary to take several drops for the reaction. When colorless, freshly redistilled quinoline is used, the reaction can detect 0.1 mg of dichloroethane.

Dichloroethane vapor can be detected in the atmosphere by passing the air through a glass tube 10-12 cm long and 0.5 cm in diameter, containing glass wool and a plug of 2-3 cm length of dry, finely crushed silica gel, particle size 1 mm. For a considerable concentration of dichloroethane, more than 1 mg/l, it is sufficient to pass 1-2 liters of air. If the dichloroethane content is low, then a greater volume of air has to be passed through. The tube is moistened with a

few drops of quinoline and heated on an electric hot plate.[1] If the grains of silica gel redden after 2-3 minutes, the presence of dichloroethane in the air is confirmed. In the absence of dichloroethane the silica gel remains colorless.

Selectivity of the Reaction

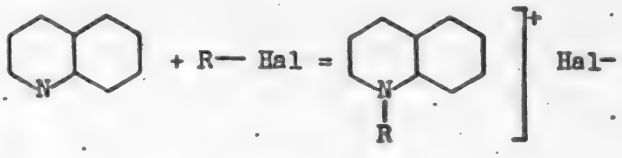
The following compounds do not give this reaction and no color is formed with quinoline. Hydrocarbons: benzene, toluene, xylene, gasoline, kerosene; halogenated hydrocarbons: chloroform, 1,1-dichloroethane (ethylene chloride, CH_3-$CHCl_2$), carbon tetrachloride, chlorobenzene, chloronaphthalene, polychloronaphthalenes (Halovaks); alcohols: methyl, ethyl, propyl, butyl, amyl alcohols; esters: amyl acetate, butyl acetate, ethyl acetate; ethers: diethyl, diisopropyl; acids: acetic, pyridine.

In addition to 1,2-dichloroethane the following give positive reactions with quinoline; ethyl bromide, 1,2-dibromoethane; ethyl iodide, ethyl chloride. Nevertheless we have never come across the use of the halogenated hydrocarbons just enumerated as solvents or as components of mixtures with dichloroethane either in practice or in the literature.

A Proposed Mechanism for the Reaction

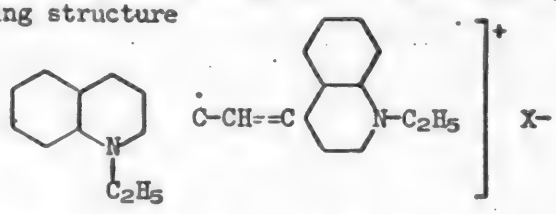
Investigations already carried out and still in progress enable us to propose the following mechanism for the reaction.

By the action of alkyl halides, quinoline, like any other tertiary amine, forms salts of a quaternary ammonium base;



the different alkyl halides react at different rates.

Quaternary quinoline salts on heating with alkaline solutions form intensely colored cyanine dyes, e.g. with ethyl iodide quinaldine, and quinoline forms a dye of the following structure



which gives solutions of an intense rose color. Dyes of this class have been studied extensively. There are a number of investigations and patents, describing methods of preparation and the properties of this class of dyes [6,7]. It has been pointed out also that analogous dyes are also formed from quinoline and alkylquinoline salts without participation of the alkyliodides of quinaldine and lepidine [8].

In this case the ease of conversion of quaternary quinoline salts into colored products also depends on the nature of the alkyl group. According to the nature of the alkyl radical which participates in the formation of colored compounds, the temperature and alkalinity of the medium must be varied.

The red products formed as a result of the color reaction for dichloroethane possess all the properties of cyanine dyes obtained from salts of methyl or ethyl quinoline. These products dissolve with the same red color in dilute

[1] It is important that the tube not rotate. When heat is applied to one side only, the heating proceeds nonuniformly, and there will always be found in the tube a region of nearly the optimum temperature.

acids and have colored cations, which are precipitated under the influence of large complex anions, such as HgI_4^{2-}, $Zn(SCN)^{2-}$, CdI_4^{2-}, etc. In a number of these cases typical "colored solid phase reactions" develop [9]. The behavior of the colored products formed during the reaction for dichloroethane on heating and to oxidizing or reducing agents and to other various reagents is also similar in all respects to the behavior of cyanine dyes to the same reagents, etc. It is permissible therefore to assume that cyanine dyes are formed during the reaction described.

The reason for the unexpectedly high selectivity of the reaction can only be explained by means of such a hypothesis. It is possible that 1,2-dichloroethane, in contrast to chloroform, 1,1-dichloroethane, chlorobenzene, carbon tetrachloride and others, gives the reaction because it either forms quaternary ammonium salts more easily than the others, or the salt is more easily converted into a dye, the alkalinity of the quinoline itself being high enough for the conversion.

The study of the reaction mechanism is being continued, together with work on the use of this new reaction for the quantitative determination of dichloroethane.

SUMMARY

When 0.2–0.3 ml of quinoline is heated in a test tube to boiling with a drop of 1,2-dichloroethane or a solvent which contains dichloroethane, an intense red color develops; 0.1 mg of dichloroethane can be detected by this reaction.

The reaction is highly selective; 1,1-dichloroethane, chloroform, carbon tetrachloride, various hydrocarbons, and many other substances enumerated above do not give this reaction.

The red color developed is apparently the result of the formation of cyanine dyes.

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REACTIONS FOR THE IDENTIFICATION OF DICHLOROETHANE

V. A. Nazarenko and N. V. Lapkina

It is sometimes necessary in practice to identify 1,2-dichloroethane. If a few drops of liquid are available for test then no special difficulty arises, since its characteristic smell, the determination of physical constants (specific gravity, b.p., etc), together with some simple chemical tests (determination of organically bound Cl etc), lead to a fairly complete identification of the product. It is considerably more difficult to solve the problem of identification when the internal organs (e.g. the stomach and its contents) are examined, and the distillate obtained for the determination of volatile poisons analyzed. In distillates of this kind, the dichloroethane, if present in small amounts, can be completely in solution in the water (the solubility of 1,2-dichloroethane at 20° is 0.869 g/100 ml). Similarily the vessel containing the liquid which has given rise to poisonous effects may contain such a small amount of the poison that the determination of physical constants is out of the question. The odor which resembles that of chloroform, in the absence of positive reactions for chloroform and in the presence of organically combined Cl can hardly be regarded as a reliable test for the identification of dichloroethane. The need therefore exists for a chemical reaction which can be used for the identification of dichloroethane, which is sensitive enough for application to aqueous solutions and which will enable dichloroethane to be distinguished at least from the most common chlorinated solvents, chloroform, carbon tetrachloride and trichloroethylene.

No characteristic chemical reaction is known for 1,2-dichloroethane in aqueous solution which can be used for distinguishing it from other chlorinated derivatives of methane and ethane. Nevertheless it can be converted into other compounds - ethylene glycol, acetylene and ethylendiamine, which can easily be identified by well known chemical reactions.

In the present article the possibility of detecting dichloroethane by its conversion into other compounds is considered.

1. Detection of Dichloroethane by the Formation of Ethylene Glycol

1,2-Dichloroethane is slowly hydrolyzed by water, with the formation of ethylene glycol. The reaction velocity increases considerably in the presence of Na_2CO_3, particularly on heating under pressure. Ethylene glycol in turn can be detected by the formation of formaldehyde when reacted with acid periodate solution. Finally formaldehyde is detected by Schiff's reagent. This reaction occurs not only with pure dichloroethane but also its aqueous solution.

Procedure. 0.5 ml of the aqueous test solution is introduced by means of a pipette into a 1 ml glass ampoule; this is followed by the addition of 0.5 ml of a 10% solution of Na_2CO_3. The ampoule is sealed and placed for 1 hour on a steam bath. After cooling, the ampoule is opened and the liquid transferred by means of a pipette into a small test tube. 6-7 drops of H_2SO_4 (1:8) are added until the solution is acid and then 2 drops of a 5% solution of K or Na periodate 1 N H_2SO_4 added and left for 5 minutes. Finally a saturated solution of H_2SO_3 is added until the iodine which initially separates out disappears, 2 drops of Schiff's reagent added. The appearance of a rose color indicates the presence of dichloroethane. For small amounts of dichloroethane the color only appears after

10-25 minutes. A color which develops only after 35-40 minutes should be ignored.

By this method it is possible to detect 0.4 mg of dichloroethane in aqueous solution at a dilution of 1:1200.

2. Detection of Dichloroethane by the Formation of Acetylene

Vinyl chloride is formed by the action of strong caustic on 1,2-dichloroethane. If the reaction is carried out in a closed vessel under pressure, then a further conversion of the vinyl chloride to acetylene takes place. The acetylene formed can then be detected by reacting it with an ammoniacal solution of Cu [1]. The reaction is given by aqueous solutions of dichloroethane.

Procedure. 0.5 ml of the aqueous solution of dichloroethane is introduced into a 1 ml ampoule and 0.5 ml of 20% KOH added by means of a fine capillary tube, so that as far as possible the liquids do not mix. The ampoule is sealed, the liquids mixed by shaking and then heated on a steam bath for 30 minutes. When it is cold again the ampoule is opened and the liquid transferred into a test tube by means of a pipette. A 20% acetic acid solution is added dropwise to the contents of the test tube until the solution is acid to litmus, when 2 drops of an ammoniacal solution of Cu are added. If 1,2-dichloroethane is present, a red or cherry-red color or brown and gradually a precipitate of the same color settles out. 0.25 mg of 1,2-dichloroethane at a dilution of 1:2000 can be detected in this way.

The ammoniacal solution of Cu is prepared by dissolving 1 g $CuNO_3$ and 4 g of hydroxylamine hydrochloride in a small amount of water, 5 ml of 20% ammonia is then added to the solution obtained and the whole shaken until the solution is colorless when it is made up to 50 ml with water.

3. Detection of Dichloroethane by the Formation of Ethylenediamine

When 1,2-dichloroethane is heated with a concentrated solution of ammonia under pressure, ethylenediamine is formed. The ethylenediamine can be detected by a microcrystalloscopic reaction with potassium bismuth iodide with which it forms characteristic rod shaped crystals of a bismuth iodide complex. Since polyamines are also formed during the reaction between 1,2-dichloroethane and ammonia, other crystals can be seen under the microscope besides the rod shaped ones, viz., rectangular and square shaped crystals. This reaction is only applicable to liquid dichloroethane, it cannot be used for aqueous solutions.

Procedure. A drop of dichloroethane (0.001-0.005 g) is introduced into a 1 ml ampoule and 0.5 ml of a 25% ammonia solution added, after which the ampoule is sealed, and heated on a steam bath for 1 hour. When cool the contents are transferred into a small beaker and evaporated to dryness. The residue is dissolved in two drops of water. To a drop of the solution a drop of potassium bismuth iodide is added. At first an amorphous suspension is formed which gradually crystallizes out as blood red crystals in the form of short rods, squares, and rectangles, and aggregates of these respective forms.

4. The Specificity of the Reactions for 1,2-Dichloroethane

The three reactions described above were tested on different halogenated derivatives of methane and ethane. Results are given in the table for tests carried out with both aqueous solutions and with small amounts (3-10 mg) of liquid or gaseous halogenated derivatives. From the table it may be observed that the formation of ethylenediamine and ethyleneglycol for a series of halogen derivatives of methane and ethane is specific for 1,2-dichloroethane. Allyl bromide gives a very definite reaction with the Schiff's base, probably as the

result of the formation of allyl alcohol during saponification with Na_2CO_3, the allyl alcohol on oxidation with periodate yielding formaldehyde. It should be noted that the samples of 1,1-dichloroethane and 1,1,1-trichloroethane which we tested also gave a weak positive reaction for ethyleneglycol, but this can probably be explained by the presence of small amounts of 1,2-dichloroethane in them, since the intensity differed for different samples and diminished in proportion to the extent of purification of these substances by fractional distillation.

The formation of acetylene is less specific than the other, since 1,1-dichloroethane, 1,1,2-trichloroethane behave similarily to 1,2-dichloroethane. 1,1,1,1-Tetrachloro- and tetrabromoethane, tribromoethylene and acetylene chloride under the same conditions give a profuse yellow turbidity, which on long standing for many hours changes into a red, flocculent precipitate characteristic of copper acetylide.

No.	Compound	Reaction for Formation of		
		Ethyleneglycol	Acetylene	Ethylene-diamine
1	Chloroform	–	–	–
2	Carbon tetrachloride	–	–	–
3	Monochloroethane	–	–	–
4	1,1-dichloroethane	–	+	–
5	1,2-dichloroethane	+	+	+
6	1,2-dibromoethane	+	+	+
7	1,1,1-trichloroethane	–	–	–
8	1,1,2-trichloroethane	–	+	–
9	1,1,1,2-tetrachloroethane	–	–	–
10	1,1,2,2-tetrachloroethane	–	Yellow turbidity	–
11	1,1,2,2-tetrabromoethane	–	Ditto	–
12	Pentabromoethane	–	–	–
13	Hexachloroethane	–	–	–
14	Tribromoethylene	–	Yellow turbidity	–
15	Acetylenedichloride	–	Ditto	–
16	Chloral	–	–	–
17	Bromally	+	–	–

5. How to Distinguish Between 1,2-Dichloroethane and 1,2-Dibromoethane

1,2-Dibromoethane, like 1,2-dichloroethane, gives all the three reactions described above: in order to distinguish between them the reactions for chloride and bromide are used. A drop of the liquid halogen derivative, or 0.5 ml of an aqueous solution of it, is heated with 0.5 ml of 25% ammonia in a sealed ampoule on a steam bath for 1 hour as described above for the formation of ethylenediamine. The liquid obtained is then evaporated to dryness in a small beaker and the residue dissolved in two drops of water. One drop is used for a chloride reaction with diphenylcarbazide after separation of the chromyl chloride, and the other drop for a fluorescein test for bromide.

SUMMARY

1,2-Dichloroethane can be identified by means of three reactions: 1) by conversion into ethyleneglycol by heating with Na_2CO_3 under pressure. Ethylene glycol is subsequently identified by the formation of formaldehyde by oxidation of the glycol with periodate.

2) Conversion into acetylene on heating with NaOH under pressure, the acetylene being identified by the formation of Cu acetylide. 3) Conversion into ethylendiamine on heating with ammonia; the ethylenediamine is detected by a reaction with potassium bismuth iodide.

The first two reactions can be used for the detection of 1,2-dichloroethane in aqueous solutions. The sensitivity of the first reaction is 0.4 mg (1:1200) and of the second 0.25 mg (1:2000).

The formation of ethylene glycol and ethylendiamine is specific for 1,2-dichloroethane from a series of ethane and methane halogen derivatives tested.

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RAPID METHODS OF MICROELEMENTARY ANALYSIS

V. A RAPID METHOD FOR THE DETERMINATION OF CARBON AND HYDROGEN

M. O. Korshun

Organic Microanalytical Laboratory of the Institute of Organic Chemistry, Acad. Sci., Moscow

In previous papers we have described a new, rapid method for the micro and semi-micro determination of carbon and hydrogen [1], in which we showed that it is possible to carry out a quantitative combustion of a substance in a large excess of oxygen without the use of oxidizing agents and catalysts, but under such conditions that a preliminary pyrogenetic decomposition of the substance is ensured with almost complete exclusion of oxygen. If this method is used without the use of preliminary pyrolysis, a quantitative oxidation of the organic compound is impossible.

From these experiments it became clear to us that the method of decomposition of an organic compound can play an essential role in the determination of carbon and hydrogen.

Combustion of an organic compound in an empty tube, in which only gaseous oxygen is used, enables us to pose the question as to the part played by the method of decomposition in influencing the path taken by the oxidation, i.e. to examine more closely the process of decomposition during an analysis. To solve such a problem experimentally by means of tubes containing 'universal' packings is of course impossible.

In fact, the attention of analytical chemists concerned with micro analytical determinations of the elementary composition of organic compounds, has been concentrated on the quantitative oxidation of substances by combustion mainly at the expense of solid oxidizing agents and catalysts in the presence of oxygen or air, and the question of the part played by the method of decomposition used has never been touched upon.

E. G. Weygand [2], in considering the micro analytical determination of carbon and hydrogen, came to a completely erroneous conclusion.

In 1948 Weygand wrote that the possibility of combustion analysis of organic compounds in the presence of catalysts "looked very attractive". But the author encountered difficulties during catalytic combustion of compounds and therefore concluded that "oxidation by the means of chemical methods is always more reliable" by which he meant the use of an "universal' filler for the combustion tube, as proposed by Pregl. This consists of CuO, $PbCrO_4$, PbO_2, Ag, and asbestos. Weygand however warned that only the Ag can be regarded as being above suspicion with regard to purity, while asbestos, CuO, and $PbCrO_4$ possess considerable disadvantages. Completely reliable CuO and $PbCrO_4$ are not available. In spite of this, Weygand prefers to carry out combustions according to the Liebig-Pregl method and describes it in detail in his book. In the meantime as we have shown in earlier work [3-5] the catalytic method of combustion is more reliable than the Liebig-Pregl method.

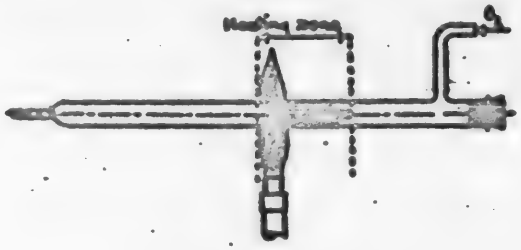
The most reliable and simple method seems to be the rapid combustion method in an empty tube. As regards the method of decomposition we are convinced that it is of considerable significance for any of the methods in existence for the determination of carbon and hydrogen. This can only be proved experimentally by combustion in an empty tube.

Observations [1] on the path taken by the decomposition of a compound when using rapid pyrolysis gave us a basis for proposing that a large part of the volatile products of thermal decomposition is oxidized almost completely on coming out of the section of the tube in the short, red hot zone of the combustion tube heated by a movable burner.

Further observations on the part played by the method of decomposition of a substance under the conditions which we worked out for the rapid method of determination of carbon and hydrogen led us to the most interesting results.

Experiments were carried out on the determination of carbon and hydrogen in certain organic compounds by means of the rapid method and the apparatus described previously [1]. The only difference was that combustion of the organic compound was effected by means of only one gas burner. No electric heater was used, and the burner used was not moved outside the zone limits marked by arrows in the diagram. The heating zone during each stage of the combustion was never more than 2-3 cm in these experiments, i.e. the width of the gas burner flame. The oxygen throughput was 35-40 ml/minute. The duration of combustion and sweeping out did not exceed 10-12 minutes. The oxygen rate indicated above was sufficient to clear away the water condensed on the cold parts of the combustion tube quantitatively.

The results obtained exceeded all expectations. From the examples adduced in Table 1 (combustion with pyrolysis) it can be seen that 95% and sometimes even 100% of the carbon contained in the test material was oxidized to CO_2, while the hydrogen in all cases was quantitatively converted into H_2O. On the other hand on carrying out the combustion in a boat under the other conditions described above, even the hydrogen was not oxidized completely (Table 2).



Scheme for Combustion

Thus it can be assumed that when the method of decomposition in a boat is used, oxidation of the material proceeds basically in that zone of the combustion tube which is heated by a long burner or an oven.

The fact that hydrogen in all the cases of combustion with pyrolysis is quantitatively converted into H_2O indicates that hydrogen is a basic product of the decomposition of a substance during pyrolysis of a compound.

The insignificant amount of carbon which is not completely oxidized to CO_2 when only one burner is used for combustion was found by us both qualitatively and quantitatively to have been converted into CO.

The results for the determination of carbon and hydrogen by means of combustion with one burner is of special interest for substance 3, Table 1, since it consists of a condensed ring with an angular methyl group. Even in such a difficult case as this where it would be expected that methane would be produced as the product of pyrolysis, we obtained theoretical values for hydrogen

and only 3.7% (absolute) less carbon than theoretical.

TABLE 1

Combustion with Pyrolysis

Compound	Wt. taken, mg	Amt. Found %		Amt Computed %		ΔC in % absol.	ΔH in % absol.	ΔC in % relative	ΔH in % relative
		C	H	C	H				
Naphthalene ($C_{10}H_8$)	5.080	92.05	6.27	93.70	6.30	-1.65	-0.03	-1.77	-0.48
	4.890	92.33	6.17	–	–	-1.37	-0.13	-0.47	-2.17
	4.345	93.67	6.23	–	–	-0.03	-0.07	-0.04	+1.02
Laevulose ($C_6H_{12}O_6$)	5.180	38.11	6.75	39.98	6.67	-1.87	-0.08	-4.68	+1.19
	4.500	35.93	6.77	–	–	-4.05	-0.10	-10.14	+11.49
9,10-(2,5-Dimethyl-2-cyclopentene-3-ol-4-one), 1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene ($C_8H_{28}O_2$)	6.580	75.96	9.07	79.67	9.15	-3.7	-0.08	– 4.66	-0.88
Methylhexahydrophthalic acid ($C_9H_{14}O_4$)	4.922	58.10	7.71	58.06	7.52	+0.04	+0.19	+0.06	+2.52
	4.022	57.76	7.70	–	–	-0.50	-0.18	-0.87	+2.39
Picric acid[1] ($C_6H_3O_7N_3$)	4.950	31.12	1.29	31.44	1.32	-0.32	-0.03	-1.02	-2.68
	4.520	30.44	1.39	–	–	-1.00	+0.07	-3.19	+5.30

TABLE 2

Combustion in a Boat

Compound	Wt. taken, mg	Amt. Found %		Amt. Computed %		ΔC in % absol.	ΔH in % absol.	ΔC in % relative	ΔH in % relative
		C	H	C	H				
Naphthalene ($C_{10}H_8$)	4.215	5.30	0.67	93.70	6.30	-88.40	-6.63	-94.35	-89.37
Methylhexahydrophthalic acid ($C_9H_{14}O_4$)	4.330	7.39	2.62	58.06	7.52	-50.67	-4.90	-87.28	-65.16

It is of interest to note that for the combustion of similar materials, six layers of filling for the combustion tube consisting of CuO and platinized asbestos are proposed in a contemporary American textbook: Niederl and Niederl [7]. If combustion of a compound were carried out with pyrolysis, then doubtless it should be possible to achieve quantitative oxidation of similar substances in the presence of only (a) a catalyst or (b) "a universal" Pregl filler even under the conditions employed in the "classical" methods of analysis.

1) Oxides of nitrogen were trapped by solid absorbents prepared according to Klimov's method [6].

By numerous experiments on combustion with one burner it was established that during the pyrolytic decomposition of an organic compound, almost complete oxidation with the use of gaseous oxygen only is achieved during the time the products of decomposition are in the very short zone heated by the gas burner and during the very short time (2-secs) when the substance is in this zone. (For a rate of 35-40 ml/minute of oxygen, a diameter of combustion tube of 9 mm and length of heated zone 20-30 mm, the contact time with oxygen is 2-3 sec.)

All the hydrogen in the molecule is oxidized to H_2O under these conditions. 95-100% carbon is oxidized to CO_2 and only up to $\sim$5% of the carbon remaining oxidized to CO.

It is obvious that subsequent oxidation in the zone heated electrically proceeds far easier than has been assumed up to the present.

It should be observed that this type of investigation on the decomposition of compounds has not been described in the literature. Apart from its theoretical interest, this investigation enables practical conclusions to be drawn, in particular the following: for a rapid determination of carbon and hydrogen a long heating zone is unnecessary, i.e., the length of the heaters and the length of the combustion tube. Thus a tube length of 33-38 cm should be sufficient instead of 62 cm and a heater length of 8-10 cm instead of 25-30 cm.

In Table 3 results are given for determinations of carbon and hydrogen in compounds of different composition and structure. Combustion of these compounds was carried out in a 36 cm tube with an electrical heater of 10 cm length at a temperature of 950°.

For the analysis of liquids of low boiling point (Table 3) we used the technique for combustion of volatile substances, described previously [1]. The combustion method used for pentane and cyclopentane was modified somewhat. In these cases aliquots were taken in a sealed capillary which was then opened in the tube. The capillary as usual was placed in an ampoule with a sealed end. That part of the tube where the widened part of the capillary is located was then cooled with ice, while its sealed end was simultaneously heated.

After the capillary had been opened, the opened end was cooled and at the same time the burner was placed at the opened end of the ampoule in which the capillary was located.

In this way we managed to get satisfactory results for pentane and cyclopentane boiling in the range 34-45°.

SUMMARY

1. It has been shown that the method used for the decomposition of a compound during combustion has an effect on the ease with which it is oxidized. Oxidation of a substance to CO_2 and H_2O (95-100%) by a pyrolytic method of decomposition is achieved in the short zone heated by a gas burner, and in the very short time, 2-3 sec., during which the material is in this zone.

2. When the rapid method for the determination of carbon and hydrogen in a large excess of oxygen is used there is no need for a large zone, i.e. for long heaters and combustion tubes. Even for analysis of volatile materials, tubes of 33-38 cm and a heating zone of 10 cm are adequate.

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TABLE 3

Compound used and empirical formula	Carbon, %			Hydrogen, %		
	Found	Computed	Diff.	Found	Computed	Diff.
10,14,17-Trimethyl-Δ^{8}-dodecahydrocyclopentanophenanthrene-3,15-dione ($C_{20}H_{28}O_2$)	79.82	79.96	−0.14	9.30	9.39	−0.09
	79.71	–	−0.25	9.28	–	−0.11
The diacetate of 3,5,7,9-tetramethylbicyclopentane-dihydroxy-$\Delta^{6,11}$-diene-1,2-dione ($C_{18}H_{22}O_7$)	61.85	61.70	+0.15	6.26	6.33	−0.07
	61.63	–	−0.07	6.23	–	−0.10
Semicarbazone 9-methyl-6-methoxy-Δ^{8}-octalone-1 ($C_{13}H_{21}O_2N_3$)	62.10	62.10	0.00	8.51	8.40	+0.11
	62.38	–	+0.18	8.22	–	−0.18
10,14,17-Trimethyl-Δ^{8}-dodecahydrocyclopentanophenanthrene-15-one ($C_{20}H_{30}O$)	83.93	83.85	+0.08	10.78	10.80	−0.02
	83.75	–	−0.10	10.68	–	−0.12
9-Methyl-1-ethinyl-1-decalol-6-one ($C_{13}H_{18}O_2$)	75.91	75.70	+0.21	8.83	8.80	+0.03
	75.88	–	+0.18	8.92	–	+0.12
2,3-Dimethylbicyclo-(2,2,2) octane ($C_{10}H_{18}$)	87.05	86.88	+0.17	13.28	13.12	+0.16
	86.98	–	+0.10	13.08	–	−0.04
17-Methyl-$\Delta^{2,16}$-1,4,8-triketotetradecahydrochrysene ($C_{18}H_{22}O_3$)	76.20	76.48	−0.28	7.53	7.43	+0.10
	76.49	–	+0.01	7.60	–	+0.17
Tri-(α-isopropoxy)-ethyl ether of triethanolamine ($C_{21}H_{45}O_6N$)	61.73	61.92	−0.19	11.17	11.06	+0.11
	61.88	–	−0.04	11.15	–	+0.09
Di-(α-isopropoxy)-ethyl ether of diethanolamine ($C_{14}H_{31}O_4N$)	60.47	60.61	−0.14	11.26	11.26	0.00
	60.41	–	−0.20	11.37	–	+0.11
1-Methyl-3-ethylcyclobutane (C_7H_{14})	85.61	85.63	−0.02	14.39	14.37	+0.02
trans-form B.p. 87.9-88.1°	85.64	–	+0.01	14.40	–	+0.03
Cis form B.p. 91-91.1°	85.56	85.63	−0.07	14.27	14.37	−0.10
	85.53	–	−0.10	14.43	–	+0.06
2-Methylpentane (C_6H_{14})	83.78	83.63	+0.15	16.33	16.37	−0.04
B.p. 58.5-59°	83.80	–	+0.17	16.44	–	+0.07
Pentane (C_5H_{12})	83.12	83.24	−0.12	16.68	16.76	−0.08
B.p. 35-36°	83.61	–	+0.37	16.95	–	+0.29
Cyclopentane (C_5H_{10})	85.33	85.63	−0.30	14.65	14.37	+0.28
B.p. 40-45°	85.20	–	−0.43	14.72	–	+0.35
1,3-Dimethylcyclobutane (C_6H_{12})	85.45	85.63	−0.18	14.53	14.37	+0.16
Trans form B.p. 57.4-57.6°	85.42	–	−0.21	14.39	–	+0.02
3-Methylpentane (C_6H_{14})	83.88	83.63	+0.25	16.36	16.37	−0.01
B.p. 60-64°	83.53	–	−0.10	16.35	–	−0.02

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RAPID METHODS OF MICROELEMENTARY ANALYSIS

VI. THE MECHANISM OF THE FORMATION OF SILVER SULFATE DURING THE SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN, AND SULFUR IN ORGANIC COMPOUNDS

M. O. Korshun

(Laboratory for Organic Microanalysis of the Institute of Organic Chemistry, USSR Acad. Sci., Moscow)

In 1948 we demonstrated the possibility of using the principle of rapid combustion for the determination of carbon and hydrogen in an empty tube for the simultaneous determination of carbon, hydrogen and sulfur on one aliquot of 4-6 mg [1].

The absorption of all the products of combustion within the limits of the tube enables one to determine any sulfur present in a compound simultaneously with carbon and hydrogen, the sulfur being trapped by metallic silver in a specially constructed apparatus. It is obvious that a quantitative determination of sulfur by the method indicated anticipates the conversion of all the "organic' sulfur by the silver to ions containing sulfur. The trapping of the oxides of sulfur by silver was first used by Dennstedt [2] in the catalytic method he developed for the determination of carbon and hydrogen.

Almost 40 years afterwards, the possibility of using this reaction between metallic silver and sulfur oxides for the quantitative determination of sulfur in organic compounds [3] was beginning to be reconsidered. Later some authors used silver for developing a method for the determination of sulfur by the catalytic combustion of a compound in a stream of oxygen. According to this method, on completion of combustion the silver is extracted from the combustion tube and the silver salt formed dissolved. Further the sulfur was determined electrolytically by weighing the silver deposited on the cathode [4] or the percentage sulfur was calculated from the loss in weight of the silver mesh after dissolving out the silver salts.

The mechanism of the reaction through which the quantitative formation of Ag_2SO_4, by the interaction of metallic silver with sulfur oxides, proceeds was up to this time unknown.

Dennstedt [2] considered that in the catalytic decomposition of organic compounds containing sulfur, the greater part reacts with silver to form Ag_2SO_4. However, this assumption is of special significance since it is only justified in those cases where the test compound contains sufficient hydrogen. Ag_2SO_4 can be obtained quantitatively even during the analysis of elementary sulfur in a stream of dry oxygen [6].

Other authors [3] in their study of the mechanism of this reaction consider it most probable that SO_3 reacts directly with heated silver, forming Ag_2SO_3 which is immediately oxidized to Ag_2SO_4 in the presence of oxygen.

This hypothesis also does not appear to be substantiated since at those temperatures at which sulfur is trapped by silver, Ag_2SO_3 is not oxidized to the sulfate, but on the other hand actually decomposes, giving SO_2 and thus losing 30% of its sulfur.

Thus, all the existing hypotheses on the mechanism of the interaction between sulfur oxides and silver seem to us to be improbable, the more so since they are derived from the assumption that Ag_2SO_4 is formed from SO_3 and silver. The formation of Ag_2SO_4 by the interaction of silver with SO_2 in general has not been mentioned. Meanwhile, during the combustion of organic compounds containing sulfur at atmospheric pressure in a stream of oxygen, the predominant formation of SO_2 or SO_3 depends on the temperature, the concentration of excess oxygen, and the presence or absence of catalysts.

According to Knietsch's results [7] on the chemical equilibrium between SO_2 and SO_3 in the presence of oxygen and platinum, 400° is the optimum temperature for 100% formation of SO_3 according to the equilibrium:

$$2SO_2 + O_2 \rightleftarrows 2SO_3.$$

None of these authors mentioned above [2-6] worked at temperatures lower than 600°, at which temperature only 80% SO_3 is formed. We worked at even higher temperatures so that the conditions in our method are not optimum for the formation of SO_3. At 950°, even in the presence of platinum catalysts, the equilibrium of the above reaction is strongly shifted to the left, i.e. towards the formation of SO_2. Consequently, under our conditions, the sulfur is most likely to be oxidized to SO_2 which, as our experimental results show, reacts afterwards with silver with quantitative formation of Ag_2SO_4.

TABLE 1

Combustion of the $C_8H_{11}O_2$ Mercaptan. Computed % S – 18.19

Wt. taken	Amount of 0.02 N I_2 used in ml	S as SO_2 %	Experimental Conditions
4.700	2.62	97.85	Combustion with one burner
7.130	3.80	93.43	Combustion with an electric furnace 10 cm long at 950°C.
6.902	1.55	38.21	Same conditions but with Pt contacts.

Such a treatment of the question disproves the hypothesis discussed above re the formation of Ag_2SO_4, only by the interaction of silver with SO_3. We have shown however precisely which oxides of sulfur react with silver in the apparatus.

In order to solve the question we carried out a series of experiments with a mercaptan (1-methoxy-5-methylhexane-5-thiol-3-one) on the assumption that under the conditions of our method, its combustion should proceed with predominant formation of SO_2.

The products of combustion in these experiments were trapped with 2 ml of 0.02 N alkali, with subsequent iodometric determination of SO_2 [8].

The results given in Table 1, show that on combustion of this mercaptan with only one burner [9] and with the use of an electric heater, 98% of all the sulfur in the molecule was obtained as SO_2, while at a temperature of 950° with a heating zone of 10 cm, in the absence of platinum contacts, 93.4% of the sulfur was found in the form of SO_2. In the presence of platinum contacts and under similar experimental conditions 38% of all the sulfur was as SO_2.

We thus established that combustion of this mercaptan with one burner leads to almost quantitative formation of SO_2 from the sulfur.

Further combustions of the same mercaptan were carried out with the inclusion of a furnace, but in which the SO_2 was trapped at 700° by silver, and the H_2O and CO_2 by the usual methods. Equally satisfactory results were obtained for carbon, hydrogen and sulfur (Table 2).

TABLE 2

Combustion of a Mercaptan: Computed %: C-54.50; H-9.16; S-18.19

Wt. in mg	Wt. CO_2 in mg	Wt. H_2O in mg	Wt. SO_4 in mg	Found %			Diff., Absol. %		
				C	H	S	C	H	S
4.133	8.234	3.462	2.218	54.37	9.37	17.91	-0.13	+0.22	-0.28
4.695	9.333	3.880	2.512	54.25	9.25	17.86	-0.25	+0.10	-0.33

The following experimentally established facts can therefore be listed:

1) The presence of H_2O is not essential to ensure that heated silver will react with sulfur oxides to form Ag_2SO_4; Ag_2SO_4 is quantitatively formed even during the combustion of elementary sulfur in a dry stream of oxygen.

2) Ag_2SO_3 is not oxidized by a stream of oxygen to Ag_2SO_4 in the absence of silver, on the other hand, at a high temperature (650°) decomposition of Ag_2SO_3 with formation of SO_3 (ca.30%) occurs.

3) Silver heated to 650-800° reacts with a mixture of SO_2 and SO_3 and hydrogen passing over it with the quantitative formation of Ag_2SO_4.

4) The formation of Ag_2SO_4 proceeds independently of whether the silver comes in contact with SO_2, or SO_3 or a mixture of the two.

These facts disprove the opinion that quantitative formation of Ag_2SO_4 can be the result only of a reaction between silver and SO_3 in a stream of oxygen.

On the basis of these experimental results we think that the following hypothesis may be advanced for the mechanism of the absorption of sulfur oxides by silver; metallic silver during combustion completely converts any sulfur oxides coming in contact with it into Ag_2SO_4, and thus seems to be a unique catalyst participating in the formation of the end products of the reaction.

SUMMARY

1. It has been established that during the combustion of compounds containing carbon, hydrogen and sulfur under our experimental conditions, the sulfur is evolved as a mixture of SO_2 and SO_3, the ratio of which is determined by the equilibrium

$$2SO_3 \rightleftarrows 2SO_2 + O_2,$$

which depends on the temperature, the oxygen content of the mixture, and other experimental factors.

2. It has been established that heated silver reacts with SO_2 and SO_3 under the conditions of the given method with quantitative formation of Ag_2SO_4. The formation of Ag_2SO_4 proceeds independently of whether the silver comes into contact with SO_2 or SO_3 or a mixture of the two.

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RAPID METHODS OF MICROELEMENTARY ANALYSIS

VII. A NEW METHOD FOR THE SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN, AND SULFUR IN ORGANIC COMPOUNDS CONTAINING C, H, O, N AND S.

M. O. Korshun and N. S. Sheveleva

(Laboratory for Organic Microanalysis, The Institute of Organic Chemistry, Acad. Sci. USSR, Moscow)

We established [1,2] that at a temperature of 750° metallic silver quantitatively traps sulfur oxides. The increase in weight of the tube containing the silver was shown to correspond exactly to the weight of SO_4 and consequently the factor for calculating S is $S/SO_4 = 0.3338$.

The accuracy of the results for sulfur determined simultaneously with carbon and hydrogen by the method we developed previously lies within the limits (0.5–1.5%). As we showed later the reason for the low results for sulfur is probably the condensation of an insignificant amount of sulfuric acid in that part of the combustion nozzle where a rubber connection was used. On changing over to an apparatus for trapping sulfur which was connected through a ground glass joint to the combustion tube, we got completely satisfactory results.

Temperature of the Silver

There are quite a number of contradictory results in the literature regarding the temperature to which the silver should be heated for quantitative trapping of sulfur oxides. Some consider that 665° is the optimum temperature. Huffmann [3] considers 350° to be the optimum temperature, but at the same time states that at 550°, silver becomes most active. Others use the silver for trapping sulfur oxides at 800° [4].

Experiments which we carried out on the determination of sulfur in toluenesulfamide, in which the sulfur oxides were trapped with silver at temperatures ranging from 420-700°, showed that particularly low values were obtained for sulfur content in the temperature range 420-600°. This lowering of the true value of sulfur decreased on increasing the temperature to which the silver was heated. The results obtained were as follows:

Temperature of silver in °C	420	500	600	700
Sulfur found %	6.0	13.0	17.54	18.73
Sulfur computed %	–	18.73		

Further observations showed that the range 650-700° may be regarded as the optimum temperature range for the quantitative formation of Ag_2SO_4 for conditions of rapid combustion in a large excess of oxygen.

We observed quantitative formation of Ag_2SO_4 at 800° also. The necessity of using such a high temperature may become apparent in the determination of C, H and S without the use of an electric furnace for the combustion tube. That it is possible to adopt such a procedure for the simultaneous determination of C, H and S in which the only oxidizing zone for the decomposition products of the test material is heated metallic silver, was demonstrated by experimental results

published previously [1]. It should be observed nevertheless that at such a high temperature the tube containing the silver becomes strongly corroded and often gets out of order. In the present work therefore we maintained an oxidizing zone in the combustion tube by means of an electric furnace, and worked at a silver temperature of not more than 700°.

TABLE 1

Determination of Sulfur in Toluenesulfamide at Different Temperatures for the Silver. Computed: 18.73%

Ag. Temp. in °C	Wt. taken in mg	Wt. SO_4 in mg	S Found in % abs.	Experimental Conditions
420	4.730	0.465	3.28	Combustion in a stream of O_2
420	3.640	0.635	5.82	at a rate of 35-40 ml^2/min,
420	8.860	2.110	11.96	length of heating zone of
520	6.070	1.695	9.32	combustion tube 10 cm at a
540	4.905	2.430	16.54	temperature of 950°C.
600	4.102	2.155	17.54	
620	4.580	2.550	18.58	
640	5.450	3.082	18.88	
700	3.636	2.060	18.91	
700	4.522	2.538	18.73	
740	5.359	2.995	18.65	

The Temperature of the Oxidizing Zone With and Without Platinum Catalysts

Since we were not interested in introducing radical changes into the methods of determining carbon and hydrogen which we developed previously, in which quantitative oxidation of compounds containing C, H, O and N proceeds in the absence of platinum contacts exclusively at the expense of a large excess of oxygen heated to 950°, then it was of interest to carry out simultaneous determinations of carbon, hydrogen and sulfur under the same conditions.

Compounds in which sulfur was in a reduced form - sulfides, mercaptans - were of special interest. It is natural that the oxidation of bivalent sulfur under our experimental conditions should be more difficult than that of sulfur in an oxidized form. Experiments with ditolyldisulfide, thianthrene, mercaptan (1-methoxy-5-methylhexane-5-thiol-3-one) and dithiane (Table 2) showed equally good results for carbon, hydrogen and sulfur both with and without platinum catalysts.

We thus established that at a temperature for the oxidizing zone of 950°, analyses could be carried out without platinum contacts. A large number of simultaneous determinations of carbon, hydrogen and sulfur in different organic compounds was made, the results of which are given in Table 3.

It is clear from these examples that equally accurate results can be obtained for sulfides, disulfides, mercaptans, sulfones and other compounds independently of their sulfur content.

Apparatus

As pointed out above, determination of sulfur by the method worked out previously could be carried out with an accuracy of from 0.5-1.5%, the low results being the consequence of the condensation of insignificant amounts of sulfuric acid at the junction of the combustion tube where a rubber connection was used [2].

TABLE 2

Simultaneous Determination of C, H and S with and without Platinum Contacts

Designation of Compound and Empirical Formula	Pt. contacts used or not	Wt. in mg	Wt. in mg			Found in %			Diff. in %		
			CO_2	H_2O	SO_4	C	H	S	C	H	S
Thianthrene ($C_{12}H_8S_2$)	No	5.170	12.620	1.760	4.610	66.62	3.81	29.76	0.00	+0.08	+0.11
Computed %:	No	6.105	14.875	2.030	5.425	66.49	3.72	29.66	-0.13	-0.01	-0.01
C-66.62;	Yes	4.940	12.110	1.700	4.390	66.90	3.35	29.66	+0.28	+0.12	+0.01
H-3.73;											
S-29.65.											
Mercaptan 1-methoxy-5-methylhexane-5-thiol-3-one ($C_8H_{16}O_2S$)	Yes	4.900	9.800	3.990	2.652	54.58	9.11	18.07	+0 08	-0.05	-0.12
	No	4.366	8.690	3.580	2.370	54.32	9.18	18.12	-0.18	+0.02	-0.07
Computed %:											
C-54.50;											
H-9.16;											
S-18.19.											
2,5-Dimethyltetrahydro-1-thiopyrylidene-4-acetic acid ($C_2H_{14}O_2S$)	Yes	4.348	9.208	3.028	2.205	57.80	7.79	16.93	-0.23	+0.21	-0.25
	No	4.957	10.550	3.345	2.530	58.08	7.55	17.04	+0.05	-0.03	-0.14
Calculated %											
C 58.03;											
H 7.58;											
S 17.18.											
Dithiane ($C_4H_8S_2$)	Yes	4.452	6.545	2.605	7.122	40.12	6.55	53.40	+0.06	-0.15	+0.26
Computed %:	Yes	5.290	7.788	3.253	8.410	40.18	6.88	53.06	-0.18	+0.18	-0.28
C-39.97;	No	5.460	8.030	3.320	8.720	40.13	6.80	53.31	-0.03	+0.10	-0.03
H-6.70;	No	4.605	6.790	2.800	7.385	40.24	6.80	53.53	+0.19	+0.10	+0.15
S-53.34.											
Ditolyldisulfide $C_{14}H_{14}S_2$	Yes	4.860	12.135	2.585	3.780	68.14	5.95	25.96	-0.10	+0.23	-0.07
	No	5.470	13.645	2.775	4.270	68.07	5.68	26.05	-0.17	+0.06	+0.02
Computed %:											
C-68.24;											
H-5.73;											
S-26.03											

It was essential therefore to construct a quartz combustion tube which could be connected with the apparatus containing silver by means of a ground glass joint.

The new model of the combustion tube which we constructed is shown in Fig. 1, in which a ground glass absorption apparatus for trapping the sulfur is included.

TABLE 3

Designation of Compound and Empirical Formula	Wt. in mg	Weight, in mg			Found %			Difference, %		
		CO_2	H_2O	SO_4	C	H	S	C	H	S
7,13,15-Trimethyl-6-thiostyrene-9(11)-one-17 $C_9H_{28}OS$ Computed %: C-17.95; H-9.27; S-10.52	5.290	14.520	4.470	1.670	74.91	9.45	10.54	-0.04	+0.18	+0.02
	5.130	14.060	4.210	1.585	74.80	9.18	10.31	-0.15	-0.09	-0.21
α-Naphthyldicyclosulfide $C_{20}H_{28}S$ Computed %: C-80.00; H-9.34; S-10.66	4.800	14.060	4.090	1.535	79.94	9.54	10.68	-0.06	+0.20	+0.02
	4.980	14.585	4.240	1.595	79.92	9.53	10.69	-0.08	+0.19	+0.03
Cyclohexyldecylsulfide $C_{16}H_{32}S$ Computed %: C-74.92; H-12.57; S-12.50	6.420	17.090	7.340	2.450	75.20	12.70	12.74	+0.18	+0.22	+0.24
	5.990	-	-	2.270	-	-	12.65	-	-	+0.15
Semicarbazone-2-methylhexahydrothiochromane-4-one $C_{11}H_{19}ON_3S$ Computed %: C-54.74; H-7.93; S-13.28	3.915	7.856	2.846	1.542	54.76	8.13	13.15	+0.02	+0.20	-0.13
	3.820	7.648	2.710	1.520	54.64	7.94	13.28	-0.10	+0.01	0.00
2,2'-Diisobutoxydiethylsulfide $C_{12}H_{26}O_2S$ Computed %: C-61.49; H-11.18; S-13.68	6.833	15.392	6.830	2.790	61.48	11.18	13.63	-0.01	0.00	-0.05
	5.070	11.424	5.074	2.059	61.49	11.20	13.55	0.00	+0.02	-0.13
2,5-Dimethyltetrahydro-1-thiopyral-4-cyanoacetic acid $C_{10}H_{13}O_2NS$ Computed %: C-56.85; H-6.20; S-15.14	5.438	11.362	3.070	2.460	57.02	6.32	15.10	+0.17	+0.12	-0.04
	5.139	10.747	2.938	2.373	57.07	6.40	15.42	+0.24	+0.20	+0.28
The amide of 2,5-dimethyltetrahydrothiopyrane-4-hydroxy-4-acetic acid $C_9H_{17}O_2NS$ Computed %: C-56.16; H-8.43; S-15.77.	4.310	8.400	3.327	2.020	53.19	8.64	15.65	+0.03	+0.21	-0.12
	3.960	7.740	3.028	1.850	53.34	8.56	15.60	+0.18	+0.12	-0.17

Table 3 (continued)

Designation of Compound and Empirical Formula	Wt. in mg	Weight, in mg			Found %:			Difference, %		
		CO_2	H_2O	SO_4	C	H	S	C	H	S
Phenlcyclopentylmercaptan $C_{11}H_{14}S$ Computed %: C-74.10; H-7.92; S-17.98	6.090	16.577	4.332	3.328	74.28	7.96	18.24	+0.18	+0.04	+0.26
	5.297	14.440	3.740	2.840	74.40	7.90	17.90	+0.30	-0.02	-0.08
α-Thionaphthol $C_{10}H_8S$ Computed %: C-74.96; H-5.03; S-20.01	4.200	11.540	1.920	2.525	74.98	5.12	20.07	+0.02	+0.09	+0.06
	4.320	11.860	1.980	2.600	74.92	5.13	20.08	-0.04	+0.10	+0.08
2-Methyl-2-3-dihydrothiopyrane dioxide $C_6H_8O_3S$ Computed %: C-44.98; H-5.03; S-20.02	6.700	11.031	3.035	3.995	44.93	5.07	19.90	-0.05	+0.04	-0.12
	5.598	9.185	2.506	3.345	44.78	5.01	19.95	-0.20	-0.02	-0.07
Bis-β-butoxyethyl-mercapto-1,1-ethane $C_{14}H_{30}O_2S$ Computed %: C-57.09; H-10.27; S-21.77	4.575	9.550	4.217	3.00	56.84	10.30	21.84	-0.25	+0.03	+0.07
	7.911	15.440	6.827	4.773	57.01	10.34	21.55	-0.08	+0.07	-0.22
Thioxane C_4H_8OS Computed %: C-46.12; H-7.74; S-30.78	4.643	7.850	3.250	4.250	46.14	7.83	30.55	+0.02	+0.09	-0.23
	4.986	8.442	3.460	4.562	46.20	7.76	30.54	+0.08	+0.02	-0.24
Vinylethylsulfide C_4H_8S Computed %: C-54.49; H-9.14; S-36.37	4.447	8.845	3.624	4.830	54.30	9.14	36.25	-0.19	0.00	-0.12
	4.000	8.770	3.550	4.775	54.39	9.03	36.30	-0.10	-0.11	-0.07
Butanedithiol-1,3 $C_4H_{10}S_2$ Computed %: C-39.30; H-8.24; S-52.46	7.190	10.360	5.295	11.300	39.32	8.24	52.46	+0.02	0,00	0.00
	4.420	6.380	3.260	6.920	39.39	8.25	52.30	+0.09	+0.01	-0.16
Dithialane-1,2 $C_3H_6S_2$ Computed %: C-33.93; H-5.69; S-60.38	3.918	4.005	1.950	7.064	34.16	5.57	60.18	+0.23	-0.12	-0.20
	7.655	9.600	3.960	13.500	34.22	5.79	60.23	+0.29	+0.10	-0.15

Both combustion tube and absorption tube were made of transparent quartz.

This type of joint seems to be stable enough in use and ensures that the apparatus is hermetically sealed during combustion. In addition, such a

combustion tube is universal, since in the absence of sulfur in the test compound, the water absorption apparatus can be directly connected by means of a rubber tube to the outlet tube, leading from the ground glass joint of the combustion tube.

This apparatus has been used successfully for over two years in our own laboratory. All experiments were carried out on this apparatus. As we established previously the length of the combustion tube can be shortened to 365 mm and that of the heating zone to 100 mm [5].

The set up for the simultaneous determination of carbon, hydrogen and sulfur is shown in Fig. 2.

The Apparatus for Sulfur Absorption. In constructing this apparatus, Fig. 1, it was borne in mind that it would have to be weighed on a micro balance. The apparatus is provided on one side with an outlet tube of internal diameter 1 mm, and on the other with a ground glass cone, by means of which it can be connected to the combustion tube. When the apparatus is weighed it is sealed by means of a hollow ground glass stopper. This type of construction eliminates the diffusion of external oxygen during weighing. The absorption tube for sulfur is weighed full of oxygen just the same as the absorption tubes for CO_2 and H_2O.

The sulfur absorption tube is filled with metallic silver through the wide opening. It is better to use silver in the form of fine ribbon, turnings or wadding, since in these forms silver has a large surface in relation to a small weight.[1)]

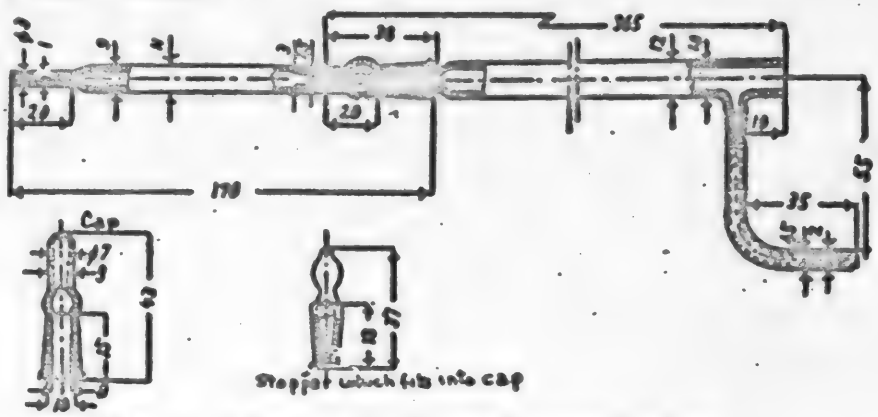

Fig. 1. A new model of the combustion tube

The weight of silver, in the form of ribbon for filling the tube amounted to 2.5–3.5 g. This amount is sufficient for 25-30 sulfur determinations, in the course of which less than a half of the silver is used, and this can be replaced.

Procedure

Before starting a run and while the electric furnaces 1, 7 and 9 (Fig.2) are heated to the requisite temperature, the absorption tube containing the silver is connected by means of its ground glass joint to the combustion tube and a short electric furnace 8-10 cm long which can be heated to 700° fitted on to it. The absorption tubes for water and carbon dioxide are then respectively fitted on and

1) We observed that the activity of the silver can be enhanced before use by reduction with methyl alcohol. The catalytic activity of silver reduced with hydrogen is considerably lower and moreover the silver loses its mechanical stability by hydrogen treatment.

a blank run made. After the blank test all the absorption tubes are weighed, the silver tube being weighed last. The tubes are then all connected up again with the combustion tube, the test sample in its ampoule introduced and combustion carried out as described previously in the method for the determination of carbon and hydrogen [6].

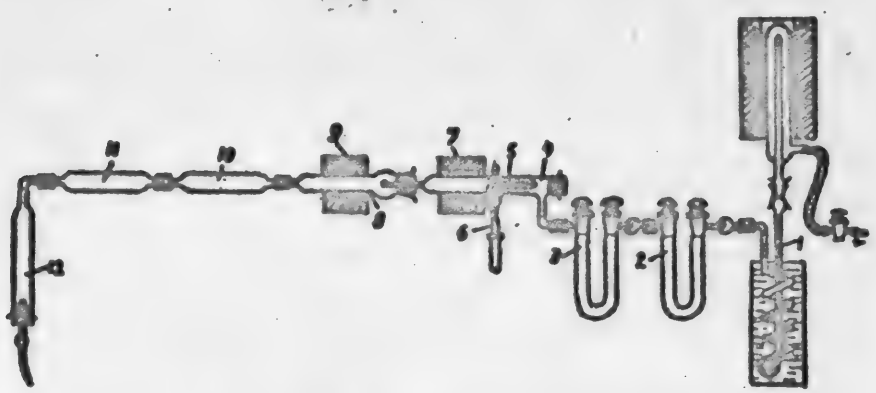

Fig. 2. Set up for the simultaneous determination of carbon, hydrogen and sulfur.

1 - Gas purifying apparatus with electric furnace; 2 - U tube with ascarite; 3 - U tube with anhydrone; 4 - quartz combustion tube; 5 - quartz ampoule for sample; 6 - burner; 7 and 9 - electric furnaces; 8 - sulfur absorption apparatus; 10 - water absorption tube; 11 - carbon dioxide absorption tube; 12 - end tube with anhydrone.

If halides are present as well as sulfur, determination of each of the elements separately is impossible. The presence of nitrogen does not interfere with the simultaneous determination of carbon, hydrogen and sulfur.

We regard it a pleasant task to express our heartfelt thanks to the Docent of the Chair of Petroleum in the Chemistry Faculty of the Moscow State University, I. N. Tits-Skvortsov, who kindly gave me a number of pure compounds for confirmatory work by the method developed.

SUMMARY

1. A new gravimetric method for the simultaneous determination of carbon, hydrogen and sulfur on one aliquot of 4-7 mg has been worked out. The accuracy of determination for the three elements is 0.2-0.3%.

2. The method consists in the decomposition of the sample by the usual method in an empty tube in a rapid stream of oxygen (35-40 ml/min) with subsequent trapping of the products of oxidation by the respective absorbents. Metallic silver is used in a special quartz tube for trapping sulfur oxides. Carbon dioxide and water are trapped as usual by means of ascarite and anhydrone respectively.

3. The optimum temperature for the quantitative absorption of sulfur oxides by silver was found to be in the range 650-800°.

Received December 20, 1950

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A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS

P. N. Fedoseev and N. P. Ivashova

(Nikolaev Shipbuilding Institute and the Nikolaev Pedagogic Institute)

Many methods are known for the quantitative determination of nitrogen in organic compounds [3,4,6-10]. The most widely used are the Dumas and Kjeldhal methods. The Dumas method is regarded as a classical method and is applied for the analysis of all organic materials containing nitrogen. The drawbacks of the Dumas method are its awkwardness, the complexity of the apparatus, and the time taken for one analysis by this method. The Kjeldhal method is widely used in factory laboratories and in some scientific-research institutes, because it enables several analyses to be made simultaneously and does not require complex apparatus.

The drawback of the Kjeldhal method is its limited field of application.

Kjeldhal's method can only be used with difficulty for the analysis of nitro-, nitroso-, azo-compounds and particularly of heterocyclic nitrogen compounds.

A new method which we have developed for the quantitative determination of nitrogen in any organic compound is described in the present article. The principle of this quantitative determination of nitrogen in organic compounds is the heating of the nitrogenous compound in an atmosphere of hydrogen with magnesium powder [1,2,5]. Under these conditions the nitrogen reacts quantitatively with the magnesium to form magnesium nitride, which on decomposition with water yields ammonia. The latter is distilled over into a standard acid solution and determined quantitatively.

The reaction between magnesium and an organic compound containing nitrogen is carried out in a test tube or glass tube. On heating, the magnesium partly reacts with the glass, forming an insignificant amount of magnesium silicide, from which on further treatment of the reaction mass with acid, gaseous, easily inflammable silicon hydride is formed. If however the reaction mass is treated with water the inflammable silicon hydride is hardly formed at all. The slight explosions which sometimes occur at the beginning of the water treatment, do not affect the accuracy of the analysis.

Magnesium powder under our experimental conditions reacts easily not only with the nitrogen of the organic compounds, but also with halogens or sulfur. This enables nitrogen, halogens and sulfur to be determined simultaneously on one aliquot. Work is in progress on these lines. It is possible to carry out 4-5 analyses in one apparatus in one day. The time required for one analysis is 1.5 hours, the accuracy being of the order of 0.2-0.3%.

EXPERIMENTAL

About 0.1-0.15 g of the organic compound is introduced into the test tube and a small layer of magnesium powder (1.5-2 cm) spread over it.

A thin glass tube a is then fixed in the tube, a does not reach right down to the bottom. More magnesium powder is then introduced almost up to the cork. A short glass tube b, the diameter of which is slightly greater than the

diameter of tube a, is fitted into the hole of the cork. The closed test tube is turned upside down and the tube a projecting from it connected with a Kipps apparatus.

Liquids for analysis are introduced in glass ampoules.

The air is expelled from the apparatus by a stream of hydrogen in the course of 10-15 minutes. After 15 minutes while the hydrogen is still being pasred, the tube a is carefully removed from the test tube, and the Kipps disconnected. A rubber tube with clips at its ends and filled with water is fitted on to tube b. The tube is filled with water to exclude aerial nitrogen from the reaction tube. The test sample is then carefully shaken so as to mix it with the magnesium. The clips on the rubber tube are opened 1-2 minutes after switching on the combustion furnace and closed after the reaction has stopped. Heating can be carried out with a gas burner.

In our work we used a specially constructed electric furnace the general features of which are shown in Fig. 2.

Fig. 1. Test tube. 1) Sample. 2) first layer of magnesium 2') magnesium. a] Glass tube for passing hydrogen; b] glass tube for expulsion of gases.

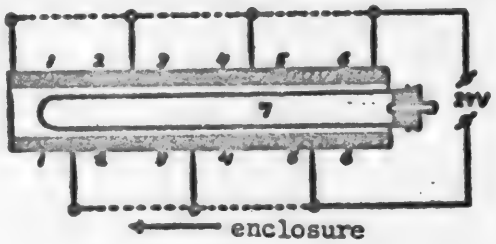

Fig. 2. Set up for electric furnace 1,2,3,4,5 and 6 - sections of the electric furnace; 7 - test tube.

The furnace consists of 4-6 sections, which can be switched on in stages. Such a set up enables the heating zone to be increased gradually as it approaches the test material.

The test tube should not be heated higher than a dark red heat (600-650°). Most organic compounds decompose completely on switching on the first two sections of the furnace (5-6 cm) at a dark red heat.

If evolution of gas is slow, the rate of heating can be increased by switching on the next section of the furnace. The combustion process can be followed by the rate of evolution of gas formed in the apparatus during decomposition of the organic compound (Fig. 3). This is achieved by immersing the rubber tube leading from the test tube in water under a cylinder or by leading it into a crystallizing basin with water.

Combustion may be regarded as complete several minutes after all the test tube has been heated to a dark red. The evolution of gas bubbles at this stage becomes very slow. Combustion should last 25-30 minutes. The test tube is cooled carefully, and broken as quickly as possible in a mortar and transferred to a 500-800 ml round-bottom flask. In order to decompose the magnesium nitride

completely 20-25 ml of 10% sulfuric acid is added. The silicon hydride which is evolved on addition of acid can ignite in the presence of air and lead to an explosion of the mixture of hydrogen and aerial oxygen. It is essential therefore that the air be expelled with carbon dioxide before addition of acid. An excess of strong alkali is finally added and the ammonia distilled over into a definite volume of standard 0.1 N hydrochloric or sulfuric acid. Distillation of the ammonia takes 30-35 minutes. Excess acid is titrated with 0.1 N alkali using methyl orange as an indicator and the nitrogen content calculated.

The results given in the table show that the accuracy is sufficient for the determination of nitrogen in organic compounds.

TABLE 1

No.	Compound tested	Molecular Formula	Calculated N, %	Found N, %	Difference
1	Nitrobenzene	$C_6H_5NO_2$	11.38	11.23	−0.15
			11.38	11.19	−0.19
2	o-Nitrotoluene	$C_7H_7NO_2$	10.21	10.03	−0.18
			10.21	10.14	−0.07
3	Nitrophenol	$C_6H_5NO_3$	10.07	10.01	−0.06
			10.07	9.77	−0.30
4	o-Nitroanisole	$C_7H_7NO_3$	11.56	11.37	−0.19
			11.56	11.36	−0.20
5	Aniline	C_6H_7N	15.04	14.85	−0.19
			15.04	15.32	+0.28
6	Toluidine	C_7H_9N	13.07	13.28	+0.21
			13.07	13.08	+0.01
7	Dimethylaniline	$C_8H_{11}N$	11.56	11.30	−0.26
			11.56	11.75	+0.19
8	Diphenylamine	$C_{12}H_{11}N$	8.28	8.25	−0.03
			8.28	8.31	+0.03
9	m-Nitraniline	$C_6H_6N_2O_2$	20.28	20.05	−0.23
			20.28	19.90	−0.30
10	p-Nitraniline	$C_6H_6N_2O_2$	20.28	20.40	+0.12
			20.28	20.38	+0.10
11	o-Nitro-p-toluidene	$C_7H_8N_2O_2$	18.41	18.15	−0.26
			18.41	18.40	−0.01
12	Ethylaniline	$C_8H_{11}N$	11.56	11.49	−0.07
			11.56	11.69	+0.09
13	Diphenylthiourea	$C_{13}H_{12}N_2S$	12.27	12.32	+0.05
			12.27	12.28	+0.01
14	Sulfanilic acid	$C_6H_7NO_3S \cdot H_2O$	6.69	6.40	−0.29
			6.69	6.52	−0.17
15	Naphthenic acid	$C_{10}H_9NO_3S$	6.27	5.98	−0.29
			6.27	6.16	−0.11
16	Azobenzene	$C_{12}H_{10}N_2$	15.37	15.24	−0.17
			15.37	15.36	−0.10

SUMMARY

1. A method is described for the quantitative determination of nitrogen in any organic compound, which is based on heating the compound with magnesium powder in an atmosphere of hydrogen.

2. The analysis is carried out in ordinary glass test tubes. One analysis takes 1.5 hours, so that 5-6 analyses could be carried out in a working day. The accuracy of the method is 0.2–0.3%.

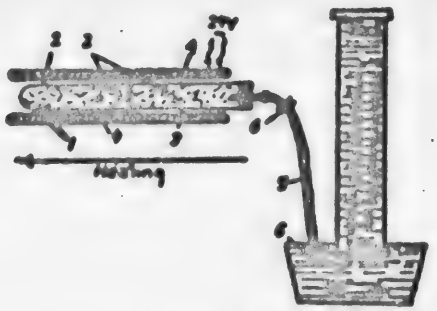

Fig. 3
1) Sample; 2) magnesium; 3) test tube; 4) furnace; 5) rubber tube; 6) clips.

3. The results obtained by the above method give us grounds for hoping that it will be widely used.

Received May 25, 1950

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A NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF SULFUR, AND FOR THE SIMULTANEOUS DETERMINATION OF SULFUR AND NITROGEN IN ORGANIC COMPOUNDS

P. N. Fedoseev and N. P. Ivashova

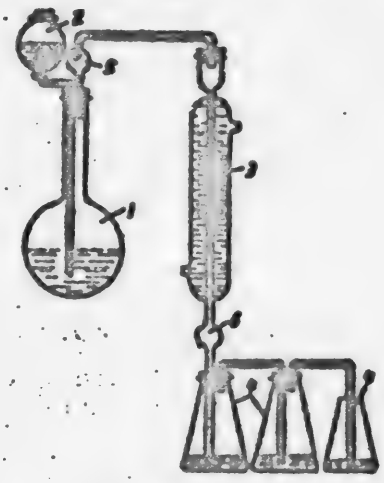
(Nikolaev Shipbuilding Institute and the Nikolaev Pedagogic Institute)

In our first paper [1] we showed that all the nitrogen in an organic compound is quantitatively converted on heating with metallic magnesium powder at 550-650° into magnesium nitride [2-10].

In this article a method is described for the determination of sulfur, and also for the determination of nitrogen and sulfur on one aliquot by the same principle. For the quantitative determination of sulfur in organic compounds, the compound is heated with magnesium powder at 550-650° for 30-40 minutes. All forms of organically bound sulfur are thus quantitatively converted into magnesium sulfide. The combustion of the organic sulfur compounds is carried out in an ordinary glass test tube. Nitrogen can also be determined simultaneously with sulfur [1]. In this case magnesium nitride and magnesium sulfide respectively are formed. On acid treatment an ammonium salt and hydrogen sulfide are formed. The hydrogen sulfide is determined iodometrically and by addition of strong alkali to the flask after removal of the hydrogen sulfide, the ammonia can be distilled over into standard acid solution and determined by back titration of the excess acid with alkali.

Combustion (30-35 minutes) of an aliquot of the test compound is carried out as described in the previous article. The test tube and its contents are ground up and transferred to a 500 ml round bottom long necked flask containing 50-80 ml of distilled water.

A stream of carbon dioxide is passed through the apparatus (see diagram) in order to expel the air, in the presence of which, on addition of acid, an explosive mixture can be formed which can be ignited by the silicon hydride (which is inflammable in the presence of air). Air will also favor the oxidation of hydrogen sulfide. When the air has been expelled, a small excess (80-100 ml) of 12% hydrochloric acid is gradually added to the flask used for decomposition so as to dissolve the remainder of the magnesium and the magnesium sulfide. A large part of the hydrogen sulfide is expelled together with the hydrogen formed and is mainly absorbed in the first absorption flask, which contains 65 ml of a mixture of 10% $ZnSO_4$ and 10% CH_3COONa with 3-5 ml of concentrated acetic acid.



Apparatus for expelling air with CO_2: 1) distillation; flask; 2) dropping funnel 3) condenser; 4)receivers; 5) splash head; 6) safety space.

The second and third absorption flasks contain 50 and 25 ml of the same mixture respectively. After all (or almost all) the magnesium has dissolved, the flask is heated for 20-25 minutes to drive over any residual hydrogen sulfide with steam. In all 70-80 ml of liquid is distilled over. When all the hydrogen sulfide has been driven over, 25 ml of 0.1 N iodine is added to the contents of the

first two absorption flasks and acidified with a few drops of 12% hydrochloric acid. After standing for three minutes the excess iodine is titrated with thiosulfate.

Results of the determination of sulfur in a number of organic compounds are given in Table 1. They show that the analytical error lies within the range 0.2–0.3%.

TABLE 1

Molecular Formula of Compound and Designation	S %			N %		
	Computed	Found	Diff.	Computed	Found	Diff.
Sulfosalicylic acid ($C_7H_6SO_6 \cdot 2H_2O$)	12.61	12.71	+0.10			
	12.61	12.69	+0.08			
Sodium alizarinsulfonate ($C_{14}H_7O_7SNa$)	9.37	9.20	−0.17			
	9.37	9.27	−0.10			
Sodium p-toluenesulfonate ($C_7H_7O_3SNa \cdot 2H_2O$)	13.92	13.65	−0.27			
	13.92	13.63	−0.29			
Bis-(1,1-dimethylpentene-3-one-sulfide ($C_{14}H_{24}O_2S$)	12.60	12.50	−0.10			
	12.60	12.54	−0.06			
Acetothienone (C_6H_6OS)	25.25	25.28	+0.03			
	25.25	25.21	−0.04			
Ditolylsulfide ($C_{14}H_{14}S$)	14.96	14.81	−0.15			
	14.86	14.69	−0.17			
Naphthenic acid $\left(C_{10}H_9NSO_3 \cdot \frac{1}{2} H_2O\right)$	13.[illegible]	14.04	+0.23	6.03	6.13	+0.10
	13.[illegible]	13.75	−0.06	6.03	6.16	+0.13
Sulfanilic acid ($C_6H_7O_3SN \cdot 2H_2O$)	15.32	15.30	−0.02	6.69	6.50	−0.19
	15.32	15.11	−0.21	6.69	6.73	+0.04
p-Toluenesulfamide ($C_7H_9SO_2N$)	18.72	17.51	−0.21	8.18	7.98	−0.20
	18.72	18.48	−0.24	8.18	7.89	−0.29
o-Toluenesulfamide ($C_7H_9SO_2N$)	18.72	18.56	−0.16	8.18	8.00	−0.18
	18.72	18.53	−0.19	8.18	8.01	−0.17
Diphenylthiourea ($C_{13}H_{12}N_2S$)	14.04	14.23	+0.19	12.27	11.98	−0.29
	14.04	14.15	+0.11	12.27	11.99	−0.28
p-Methoxyphenyl-pseudohydantoic acid ($C_{10}H_{12}O_3N_2S$)	13.34	13.16	−0.18	11.66	11.86	+0.20
	13.34	13.39	+0.05	11.66	11.66	0.00
Sodium sulfanilate ($C_6H_6NSO_3Na \cdot 2H_2O$)	13.37	13.94	+0.07	6.06	5.90	−0.16
	13.87	13.80	−0.07	6.06	5.96	−0.10
N-Methylbenzanilide-o-methylsulfide ($C_{15}H_{15}SNO$)	12.46	12.67	+0.21	5.44	5.30	−0.14
	12.46	12.23	−0.23	5.44	5.59	+0.15
2-(p-aminobenzenesulfamidopyridine) ($C_{11}H_{11}O_2N_3S$)	12.86	12.66	−0.20	16.85	16.60	−0.25
	12.86	12.63	−0.23	16.85	16.68	−0.17
4-Sulfanilylsulfanilamide ($C_{12}H_{13}O_4N_3S_2$)	19.59	19.48	−0.11	12.83	12.74	−0.09
	19.59	19.44	−0.15	12.83	12.67	−0.16
2-(p-Aminobenzenesulfamidothiazole) ($C_9H_9O_2N_3S$)	25.11	24.88	−0.23	16.46	16.26	−0.20
	25.11	25.02	−0.09	16.46	16.34	−0.12
2-Sulfanilamido-4,6-dimethylpyrimidine ($C_{12}H_{14}O_2N_4S$)	11.52	11.29	−0.23	20.13	20.00	−0.13
	11.52	11.40	−0.12	20.13	19.93	−0.20

For simultaneous determination of sulfur and nitrogen in organic compounds, combustion is carried out in the same way as for the separate determination of sulfur and nitrogen [1].

The residue after combustion of the organic compound with magnesium is transferred into a flask for decomposition. It is recommended that the sulfur be determined first by the method and in the apparatus described already (Fig.2).

When the hydrogen sulfide has been removed, the receivers for the hydrogen sulfide are removed and flasks containing standard acid (hydrochloric or sulfuric acids) for absorption of the ammonia substituted instead. The condenser and Kjeldhal set up are washed out while the two sets of flasks are being interchanged. Finally by means of a separating funnel, 50-60 ml of 50% alkali is added to the contents of the flask and the ammonia distilled over.

Results for simultaneous determinations of sulfur and nitrogen are given in Table 1.

In addition we determined total sulfur in a number of coal samples, kindly given us by the Moscow All Union Scientific Research Thermo-Technical Institute, for which we wish to express our thanks to the chief of the Heat Laboratory of the Institute, Comrade Zikeev. The results which are given in Table 2 show that our method is suitable for the quantitative determination of sulfur in coal.

TABLE 2

Coal Used	% S found in the Labs. of VTI[1]	% S found in the Labs. of NKI[2]	Diff.	No. of the VTI[1] Analysis
Coal "T"	2.93 2.93	2.79 2.65	-0.14 -0.28	5617
Podmoscovni	3.48 3.48	3.30 3.25	-0.18 -0.23	5771
Silesian	2.23 2.23	2.04 2.98	-0.19 -0.25	5753
Coal "PS"	0.98 0.98	0.95 0.86	-0.03 -0.12	5640
Anthracite "ARSh"	1.93 1.93	1.64 1.68	-0.29 -0.24	5644
Komarovsk (Podmos.)	4.98 4.98	4.95 4.94	-0.03 -0.04	6364
Angrensk	2.70 2.70	2.73 2.80	+0.03 +0.10	6694
Donets	5.14 5.14	5.27 5.02	+0.13 -0.12	6372
Anthracite "ARSh"	4.35 4.35	4.46 4.51	+0.11 +0.16	4907
Brown Coal Dust	1.68 1.68	1.65 1.60	-0.05 -0.08	6545

[1] VTI - F. E. Dzerzhinskov All Union Scientific-Research Thermotechnical Institute.
[2] NKI - Admiral S. O. Makarova Nikolaev Shipbuilding Institute.

SUMMARY

1. A quantitative method for the determination of sulfur and for the simultaneous determination of nitrogen and sulfur in organic compounds is proposed.

2. The accuracy of the method lies in the range ± 0.2 – 0.3%. The results of analyses gives grounds for hoping that the given method may be used in a number of scientific-research and factory laboratories. Comparative results for the determination of total sulfur in different samples of coal carried out by the authors and the All Union Scientific Research Institute, give good agreement.

3. The method of determination is simple, generally applicable, does not require complicated apparatus, and gives reliable results.

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SALICYLALAMINES IN ANALYSIS

4. TRICYCLIC INNER COMPLEX SALTS OF COPPER AND NICKEL

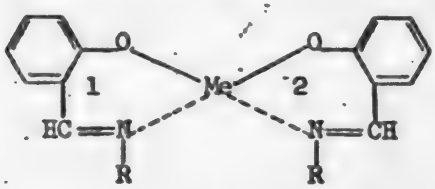
A. P.Terentyev, E. G. Rukhadze and Z. A. Fadeeva

(Lomonosov Moscow State University)

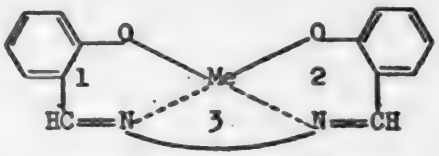
In previous papers [1] we considered the changes in the physico-chemical parameters and analytical properties of a series of Cu^{2+} and Ni^{2+} salts of the simplest homologs of the salicylalalkyl amines. The structure of the "analytical junction" in the metallic derivatives of these compounds remains unchanged, as was to be expected for the homologs. Physico-chemical properties change uniformly. The analytical character also changes very little basically.

In the present paper we shall consider the changes in the analytical parameters as a result of the effect of radical regrouping of the "analytical junction". By the term "analytical junction" we mean that system of atoms which is made up from the specific groups of molecules of the reagent and the atoms or atoms of the metal to be determined [2].

The compounds under consideration are the condensation products of salicylaldehyde with aliphatic and aromatic diamines-disalicylaldiamines. These compounds form "analytical junctions" with bivalent metals, which are composed of three mutually connected metal-rings (II) and not two rings as was the case with salicylalmonoamines (I)

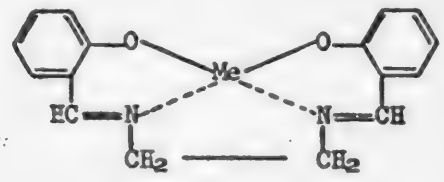


I

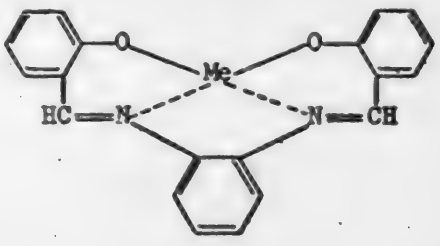


II

The effect, in the first place, of the valency structures, and secondly of the stereochemical characteristics of this third ring can become manifest to its fullest extent only during the formation of a complete analytical form. The first, obviously, is most clearly shown on comparison of the properties of the inner complex salts of Cu^{2+} and Ni^{2+} for disalicylalethylenediamine on the one hand (III) and for disalicylal-o-phenylendiamine (IV) on the other.



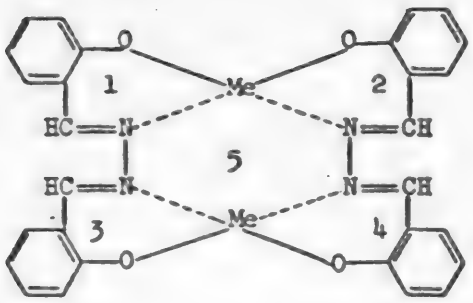
III



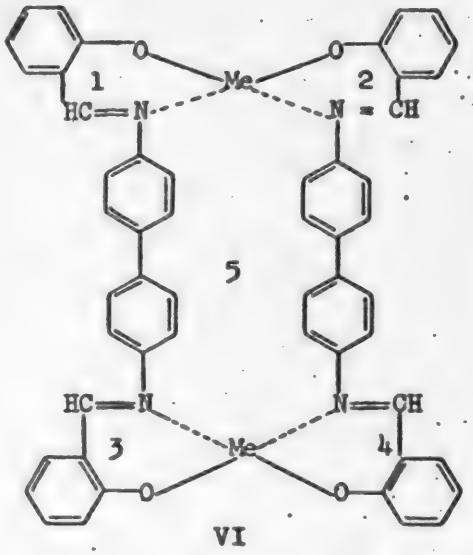
IV

The interaction between the original rings will be greater in the case of (IV) with an unbroken system of strained bonds than in the case of (III). One would expect a considerable difference in similar systems with regard to their stability, fusibility, solubility and particularly color.

The stereochemical effect could be manifested during attempts to form the third ring of the "analytical junction" as a sterically "awkward" system. Thus disalicylalazine, the reaction product of salicylaldehyde and hydrazine, should form an "analytical junction" with highly strained three-membered rings with Cu^{2+} or Ni^{2+}. The existence of a simple ring for salts of disalicylal-p-phenylenediamine and disalicylalbenzidene is impossible. In these cases one would expect the formation of a double system of a complex five-ring junction with two metal atoms (V,VI).



V



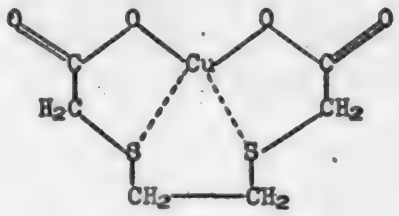
VI

Pfeiffer [3] studied similar types of inner complex salts of Cu^{2+} and Ni^{2+} in 1936; he determined the molecular weights of the copper salts of different disalicylaldiamines and thereby confirmed the formation of bimetallic five membered rings. For the syntheses of these inner complex salts it is natural to use an excess of the metal salt; when analytical precipitation is carried out, the formation of the complex salt proceeds under conditions where there is a deficiency of metal ions, since an excess of the reagent-precipitant is used. When using disalicylaldiamines therefore, as reagents, it would be natural to expect anomalies in the quantitative composition and the character of the precipitates. It is obvious that monometallic (i.e. containing one metal atom) "incomplete" molecules will be present and not only dimerization, but linear polymerization, which is so characteristic for "long" molecules, will occur. In this case this will be reflected in the character of the precipitate – mucilegenous instead of crystalline.

Thus the study of the interaction of disalicylaldiamines with metallic ions is of great interest for the theory of organic reagents. As in previous work, for better comparison we used the same cations Cu^{2+} and Ni^{2+}, for which the functionally-analytical grouping of the salicylalamines studied by us is particularly characteristic.

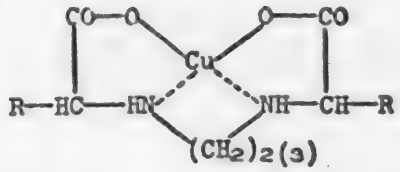
Inner complex salts with three mutually connected metal rings have been known for a long time. In 1916, Tiberg [4] prepared a number of the tricyclic

salts of Cu^{2+}, Cu^{+}, Pt^{2+} and Ag^{+}. The neutral copper salt of ethylenethioglycolic acid (VII), which is prepared by the action of sodium ethylenthioglycolate on an aqueous solution of a copper salt is a typical example of these salts.



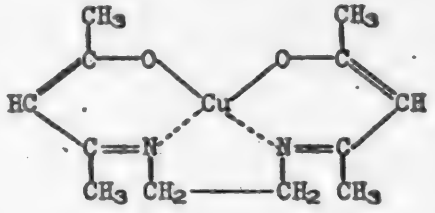
VII

Shlezinger [5] obtained various salts of ethylene and trimethylene-α-imino acids. All these salts have the following structure (VIII):



VIII

Morgar and Smith [6] by the action of acetylacetone and ethylenediamine on salts of Cu^{2+} and Co^{2+} obtained the ethylendiamino biacetylacetonates of copper and cobalt (IX):

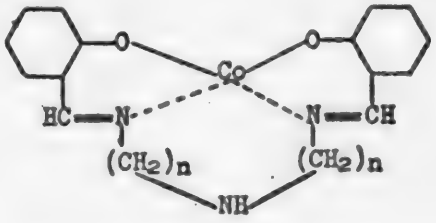


IX

Pfeiffer and coworkers [7] made more profound and wider studies of the properties of these tricyclic inner complex salts. Compounds of this type were prepared by Pfeiffer from the condensation products of salicylaldehyde with aliphatic diamines of the type $NH_2(CH_2)_nNH_2$ (n = 2-10); numerous tricyclic salts were thus prepared. In accordance with stereochemical multichain rings can be formed, when the links in the system consist of mobile chains of $-CH_2$ which can withstand bending (are pliable). In the case of aromatic diamines, where mobility is absent on account of the planar structure of the aromatic nucleus, monometallic systems can only be formed by orthodiamines. Para-diamines of the type of paraphenylenediamine and benzidene can yield only more complex inner complex salts with two metal atoms. It should be noted that according to Pfeiffer's results, all of this tricyclic system with bivalent metals is in one plane.

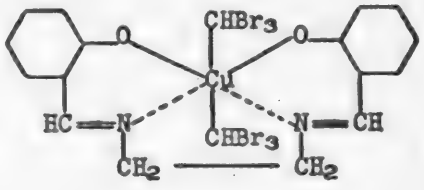
Tricyclic inner complex salts have found practical application in recent years. Thus in 1946, Calvin [8] showed that copper and zinc salicylal-o-phenylendiamines show a high specificity for neutrons. By bombardment of copper salicylal-o-phenlyendiamine with neutrons, it is possible to separate copper from other isotopes. It was also found [8] that a Co^{2+} salt of the type (X) can

combine reversibly with aerial oxygen. Such cyclic coordinately-saturated complexes should play an important part in biological oxidation-reduction processes.



(X)

Organic reagents which form tricyclic inner complex salts have not been accepted in analytical chemistry practice. There is one reference [9] to the use of a compound (XI) in luminescence analysis.



(XI)

EXPERIMENTAL

Monometallic and bimetallic tricyclic inner complex salts of Cu^{2+} and Ni^{2+} with disalicylaldiamines were isolated by us. The diamines used were of the aliphatic and aromatic series.

1. Monometallic Tricyclic Systems of Disalicylaldiamines of the Aliphatic Series

Disalicylalethylenediamine was prepared by the normal method – reaction of salicylaldehyde with ethylenediamine in the ratio 2:1 [2]. This yellow crystalline compound has a melting point of 125° and is soluble in acetone and alcohol. 1.5% solutions of disalicylalethylenediamine in alcohol or acetone precipitate Cu^{2+} in the form of green crystals and Ni^{2+} in the form of yellow-orange crystals.

Disalicylalpropylenediamine is a thick yellow oily liquid; it is soluble in alcohol, ether and acetone. A 1% alcoholic solution of disalicylalpropylenediamine precipitates Cu^{2+} in the form of a violet amorphous precipitate; and Ni^{2+} gives yellow-orange needle-like crystals.

The tricyclic monometallic salts of Cu^{2+} and Ni^{2+} with disalicylalethylendiamine and disalicylalpropylenediamine differ considerably from the salicylalmonoamines [1] in their physico-chemical and analytical parameters.

Melting Point. The tricyclic salts of Cu^{2+} and Ni^{2+} have high m.p's. They melt with decomposition above 200°. They differ considerably in this respect from the salicylalamines, which have lower melting points and are often oily [1].

Solubility. All the salts dissolve readily in organic solvents: pyridine, ethyl ether, ethyl acetate, chloroform, carbon tetrachloride, benzene, isoamyl alcohol, etc. The solubility of the higher homolog is considerably higher. The solutions are colored – the copper salts are either green (disalicylalethylene-

diamine salt) or violet (disalicylalpropylenediamine salt), while the nickel salts are orange-yellow. The color of the diamine salts is considerably more intense than those of the monoamines.

The solubility of the Cu^{2+} and Ni^{2+} salts in water is considerably greater than that of the respective complex monoamine salts. For comparison the solubilities of the complex salts of Cu^{2+} and Ni^{2+} with disalicylalpropylenediamine are given below.

TABLE 1

Solubility of the Cu^{2+} and Ni^{2+} Salts of Salicylalpropylenediamine

The amine condensed with salicylaldehyde	Solubility in 100 g water in mg	
	Cu^{2+}	Ni^{2+}
Propylenediamine	7.17	1.93

Sensitivity to pH. The Cu^{2+} and Ni^{2+} salts of the tricyclic derivatives of the diamines studied differ from the corresponding salts of the monoamines by their considerably greater stability to acids and bases. Thus the former are not decomposed by 0.01 N CH_3CO_2H, 0.01 N HCl, or by strong solutions of NaOH and NH_4OH. Salicylalmonoamines of Cu^{2+} and Ni^{2+} as a rule, are less stable to dilute acids and strong alkalies; the pH for precipitation of the disalicylalethylenediamines of Cu^{2+} and Ni^{2+} is 7.2, and for the disalicylalpropylenediamines of Cu^{2+} and Ni^{2+} - 6.8.

2. Monometallic Tricyclic Systems of the Disalicylaldiamines of the Aromatic Series

Disalicylal-o-phenylenediamine is easily prepared by mixing alcoholic solutions of salicylaldehyde and o-phenylenediamine in the ratio 2:1. The mixture is heated for one hour in a flask with an air condenser on a water bath. After cooling, yellow needles separate out which have a m.p. of 164°. They are soluble in alcohol, ether and benzene.

A 1% alcoholic solution of disalicylal-o-phenylendiamine precipitates Cu^{2+} in the form of an intensely brown colored precipitate; salts of Ni^{2+} with this amine are bright red needle-like crystals. Both salts dissolve readily in the ordinary organic solvents to form brightly colored solutions. The colors of solutions of the disalicylaldiamines of the aromatic series are far more intense than those of the disalicylaldiamines of the aliphatic series. The copper salt is stable to 0.01 N CH_3CO_2H and to both dilute and strong alkalies; the precipitation pH is 5.7. The nickel salts are less stable and are decomposed by dilute acids and strong alkalies - the precipitation pH is 8.0.

3. Bimetallic Systems of the Disalicylaldiamines

Disalicylalazine is obtained by the usual method from salicylaldehyde dissolved in alcohol and hydrazine hydrate (a 40% aqueous solution) in the ratio 2:1; this compound exists as colorless lustrous crystals in the form of platelets with a m.p. of 98°; it dissolves in alcohol, ether and other organic solvents.

A 1% alcoholic solution of disalicylalazine rapidly and quantitatively precipitates Cu^{2+} in the form of pale-yellow, and Ni^{2+} as yellow crystalline precipitates. As stated above disalicylalazine should form a bimetallic system with five rings. The "analytical junction" of this salt contain a strainless six membered ring, which explains its ease of formation and the considerable stability of these inner complex salts.

Cu^{2+} and Ni^{2+} disalicylalazines do not change even on heating above 150°. The m.p. (with decomposition) of the Cu^{2+} salt is 258° and of the Ni^{2+} salt 350°. Both salts are insoluble in the usual organic solvents. 1.2 mg of the Cu salt

and 0.59 mg of the Ni salts respectively, dissolve in 100 ml of water at ordinary temperatures; the pH for precipitation of the Cu^{2+} and Ni^{2+} disalicylalazines is 7-8.

Disalicylal-m-Phenylenediamine, Disalicylal-p-Phenylenediamine, and Disalicylalbenzidene are prepared in the same way as disalicylal-o-phenylenediamine. They are solid crystalline compounds. Disalicylal-m-phenylenediamine consists of dark yellow needles - m.p. 105°; disalicylal-p-phenylenediamines of orange red needles - m.p. 210°; disalicylalbenzidine of yellow green powder - m.p. 256°. All these compounds are only slightly soluble in water but dissolve in alcohol and benzene. Alcoholic solutions of these disalicylaldiamines precipitate Cu^{2+} and Ni^{2+}, but these precipitates differ from the usual ones in their external appearance - being non-crystalline and mucilagenous. Precipitation is not quantitative. Well formed inner complex salts of Cu^{2+} and Ni^{2+} with these reagents can only be prepared by taking a considerable amount of the respective neutral salt. This indicates that only in such a case is it possible to get more suitable conditions for the formation of double, bimetallic systems.

Practical Application of Disalicylaldiamines

Disalicylalethylenediamine, disalicylal-o-phenylenediamine, disalicylalazine are of no practical interest as reagents for the quantitative determination of copper, since the low solubility of these reagents often leads to high results. Nickel can be quantitatively precipitated by these reagents only in a very narrow pH range. Disalicylalpropylenediamine can however be recommended for the quantitative determination of Cu^{2+} and Ni^{2+}.

Reagent. 1) 1% alcoholic solution of disalicylalpropylenediamine and 2) a 10% solution of sodium acetate.

Determination of Copper

To a solution containing 5-25 mg Cu, 3-4 drops of methyl red or bromothymol blue are added, and 10% sodium acetate added until a yellow (or blue) color respectively is obtained. A 1% alcoholic solution of disalicylalpropylenediamine is then added dropwise with stirring; a violet precipitate is formed. The mixture is diluted to 100 ml with water and after standing for six hours, it is filtered through a filter crucible of average density. The precipitate is washed with cold water and dried at 130°. Correction factor 0.1848 (log 1, 26,670. Calculated molecular weight 343.8.

Results for determination of copper are given in Table 2.

TABLE 2

Determination of Copper with Disalicylalpropylenediamine

Expt. No.	Cu^{2+} taken in mg	Wt. Ppt. mg	Cu^{2+} found mg	Error mg	Error %
1	24.57	0.1329	24.56	-0.01	0.04
2	9.82	0.0530	9.79	-0.03	0.3

Analysis of copper disalicylalpropylenediamine

5.180 mg substance: 0.374 ml N_2 (23°,748 mm)
5.480 mg substance: 0.399 ml N_2 (22°,748 mm)
Found %: N 8.20; 8.29
$C_{17}H_{16}N_2O_2Cu$. Calculated %: N 8.15

Determination of Nickel with Disalicylalpropylenediamine

A solution containing 5-25 mg Ni^{2+} is diluted to 100 ml with water, 10-15 ml of a 10% sodium acetate solution (the color for a bromothymol-blue indicator should be pale blue) added and the mixture brought to the boil. A 1% alcoholic solution of disalicylalpropylenediamine (it is best to make a solution in methyl alcohol) is added dropwise with stirring. Orange-yellow lustrous needles are precipitated immediately. The solution is heated for a further 10-15 minutes and after standing for 3-8 hours it is filtered through a filter crucible of average density,

washed with water and dried at 110-120°. The calculating factor is 0.1731 ($\log \bar{1}$, 23830). The computed molecular weight is 339.00.

Results for nickel determinations are given in Table 3.

TABLE 3

Determination of Nickel with Disalicylalpropylenediamine

No.	Ni^{2+} taken in mg	Wt. Ppt. in g	Ni^{2+} Found in mg	Error	
				in mg	in %
1	24.43	0.1384	23.96	-0.47	1.8
2	12.21	0.0692	12.15	-0.06	0.49
3	9.77	0.0562	9.73	-0.04	0.40
4	6.10	0.0350	6.06	-0.04	0.66

Analysis of Nickel Disalicylalpropylenediamine

6.440 mg substance: 0.483 ml N_2 (22°, 752 mm)
4.720 mg substance: 0.350 ml N_2 (21°, 754 mm)
Found %: N 8.59, 8.54.
$C_{17}H_{18}N_2O_2Ni$. Calculated %: N 8.26.

Small amounts of Ni^{2+}, 1 - 0.1 mg, can be determined colorimetrically by means of a standard scale.

Reagents 1) a 1% solution of disalicylalpropylenediamine in methyl alcohol; 2) 10% sodium acetate; 3) a standard $NiSO_4$ solution - 1 ml of which contains 1 mg Ni^{2+}; 4) isoamyl alcohol (the fraction boiling point 128-130°).

Preparation of the Scale

Aliquots of the nickel solution containing 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; and 1 mg of Ni^{2+} respectively are introduced into colorimeter tubes of 70-80 ml capacity and diluted with water to 50 ml, 1.5 ml of the sodium acetate solution, 1 ml of the 1% reagent solution are added to each tube. The tubes are heated in a water bath for 15-20 minutes and then cooled with water. 5 ml of the isoamyl alcohol is added from a burette to each tube, which is then shaken and allowed to stand so that two layers separate out. Test solutions are treated in exactly the same way and the colors developed compared with the standards in direct light.

It should be noted that Co^{2+} is not precipitated by disalicylalpropylenediamine, but forms a light brown compound which is soluble in water from which it is not extracted by isoamyl alcohol.

SUMMARY

1. The changes in the analytical parameters of salicylalamines in relation to their structure and configuration of the "analytical junction" of the inner complex salts of Cu^{2+} and Ni^{2+} have been studied.

2. A number of the condensation products of salicylaldehyde with aliphatic and aromatic diamines and with hydrazine has been prepared.

3. According to the structure of the "analytical junction" these compounds form inner complex salts containing one or two metal atoms with Cu^{2+} and Ni^{2+}. The "analytical junction" of the compounds formed contains three rings (for a complex containing one metal atom) or five rings (for a complex containing two metal atoms).

4. The physico-chemical properties and the analytical character of salts of Cu^{2+} and Ni^{2+} with disalicylalazine, disalicylalethylenediamine, disalicylalpropylenediamine, and disalicylal-o-phenylendiamine, have been studied.

5. Disalicylalpropylenediamine can be used for the quantitative determination of Cu^{2+} and Ni^{2+} gravimetrically, and for small amounts colorimetrically.

6. It has been established that the tricyclic inner complex salts of Cu^{2+} and Ni^{2+}-products of condensation of salicylaldehyde with diamines – are distinguished by their considerably higher stability as compared with the corresponding salts of salicylalmonoamines.

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A NEW GROUP OF REAGENTS FOR BORIC ACID

I. M. Korenman and F. R. Sheyanova

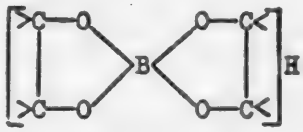
(Gorky State University)

One of us has shown previously [1] that the common property of all known organic reagents for boric acid is the capacity to form inner complex compounds with six membered rings:

Such reagents for boric acid as hydroxyanthraquinone and curcumin, which have been known for some time, possess this capacity. Rings of this type can also be postulated for derivatives of salicylic acid, which can act as reagents for boric acid. This has been confirmed experimentally [1].

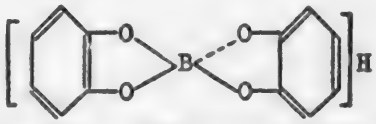
In another paper [2] it was shown that the removal of one of the atoms from the six-membered ring sometimes does not lead to a loss of the respective analytical property (i.e. of acting as a reagent for boric acid). On applying these considerations to reagents for boric acid, it can be postulated that organic compounds which lead to the formation of five membered inner complex rings of the type:

should also possess the capacity to react with boric acid. We have found references in the literature to the possibility of forming such rings. In Glebovich's article [3] the esters of boric acid with polyhydroxy compounds, to which the composition:



is assigned, are noted.

Such rings are also possible for pyrocatechol-boric acid [4] the composition of which is $[(C_6H_4O_2)_2B]H$, and to which the following structural formula can be assigned:

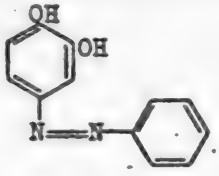
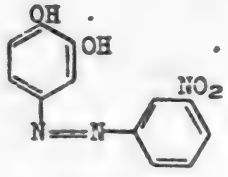
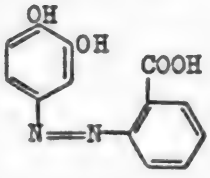
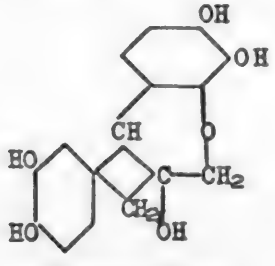


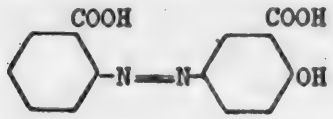
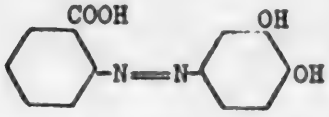
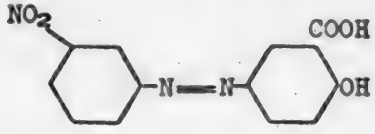
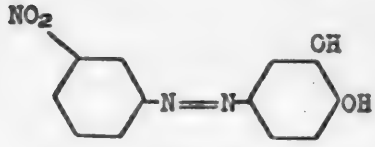
Here we have two five-membered rings. These results confirm that boron (boric acid) is capable of forming not only six-but five-membered rings. Of course pyrocatechol is not a reagent for boric acid, but colored derivatives of

pyrocatechol might be used as reagents. It should be noted that some colored derivatives of pyrocatechol have already been the subjects of research as potential analytical reagents. Kuznetsov [5] in a number of investigations used them for reactions with aluminum, gallium, thorium, zirconium, titanium, antimony and others, nevertheless the capacity of such compounds to give analytical reactions with boric acid had not hitherto been mentioned. Consequently we examined the behavior of some colored derivatives of pyrocatechol with boric acid.

After a number of preliminary tests we finally adopted the following procedure: 1-2 drops of a boric acid solution were placed in a small crucible, and 2 drops of concentrated ammonium hydroxide added to neutralize any strong mineral acids which may be present in large amounts. 1-2 drops of hydrochloric acid (1:1) was then added and the mixture evaporated to dryness on a sand bath. One drop of a saturated alcoholic solution of the reagent was added to the dry hot residue and again evaporated to dryness. The presence of boric acid is indicated by the appearance of a characteristic color, which can be easily distinguished from the color of a control test in which boric acid is absent.

The results obtained are given below.

Formula of Reagent	Color of the dry residue		Sensitivity of the reaction for boric acid	
	without boric acid	with boric acid	limit of identification	limiting conc.
	Greyish-yellow	Reddish-brown	100	1:500
	Yellowish-brown	Brick-red	2.5	1:20000
	Yellow	Violet	2.5	1:20000
 Hematoxylene	Yellow	Ditto	2.5	1:20000

Formula of Reagent	Color with Boric Acid	Limiting Conc.
	Orange	1:500
	Violet	1:20000
	Orange-yellow	1:100
	Brick-red	1:20000

We compared some of these reagents with analogous derivatives of salicylic acid [1].

It is clear that the pyrocatechol derivatives give more intense colors with boric acid than the corresponding derivatives of salicylic acid. The reactions for the pyrocatechol derivatives are also more sensitive.

SUMMARY

1. It has been shown that organic compounds which give five membered inner complex rings with boron, can be used as reagents for boric acid. It was first experimentally shown that removal of one of the carbon atoms from a six membered ring does not radically change the analytical properties of the compound.

2. It has been shown that some azodyes – derivatives of pyrocatechol and of hematoxylene, which is itself a derivative of pyrocatechol – are capable of giving fairly sensitive, color reactions with boric acid.

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CRITICISM AND BIBLIOGRAPHY

Yu. V. Karyakin. "Acid-Base Indicators". Theoretical Bases and Practical Application. State Chem. Press. 1951, 198 pp, 11 roubles 65 kopecks.

The appearance of this book is very timely. Up to now only a translation of Kolthoff's book "Application of Colored Indicators" (1929) has been available in the Russian language, and the subject matter in this book is very much dated. Karyakin's book, which is smaller, contains more new facts on the theory of acid-base indicators, their properties and applications. The book consists of an Introduction and seven chapters. In the Introduction the author analyzes the advantages and disadvantages of the colorimetric method for the determination of hydrogen ion concentration, he regards the limiting accuracy of the method as 0.01 pH units. Such an accuracy is scarcely ever attainable by visual determination of pH without the help of some apparatus. In Chapter I "The concept of the acidity of a solution", it should have been shown (page 9) that at room temperature pH + pOH = 14, since this relation enables pOH to be rapidly determined from the value of pH. It would have been useful to indicate that pH can have negative values and be greater than 14. In Chapter II the author in a concise manner deals with the behavior of electrolytes in aqueous solutions. On p. 23 in discussing the properties of buffer solutions, it should have been said that the pH of such solutions changes very little on dilution. In the same chapter in the section of "Preparation of buffer solutions", considerably more information should have been given, including information on the large number of buffer mixtures of vital practical importance. The method of making up mixture 2 contains a very serious error.

V should refer not to the solution of biphthalate but to hydrochloric acid. There are a number of smaller errors. Thus in buffer mixture 4, for a pH 6.4 - V should be 12.6 ml and at a pH 6.8 should be 23.65 ml. For the preparation of buffer mixture 12, solutions 0.4 M with respect to H_3PO_4, 0.04 N with respect to CH_3COOH and 0.04 M with respect to H_3BO_3 should be used and not equal volumes of the three solutions. In the discussion on the purification of chemicals used for the preparation of buffers, the author says nothing about the use of chemically pure reagents with respective GOST[1] numbers, e.g. Potassium biphthalate with a Gost number - GOST 5858-51 but confines himself to indicating the methods for the purification of "bought chemicals", which in the majority of cases is hardly profitable. Nothing is said about the use of hygrostats (e.g. for borax). The preparation of strong alkali solutions involving the use of ether and metallic sodium should not be recommended because of the inflammability of the ether.

The literature on this section of the book is very meagre. There is no reference to R. I. Alekseev's article in the book "Reagents and Preparations for Laboratory Purposes" under V. V. Loginov's editorship, where there is information on buffer mixtures published in the literature.

In Chapter III the author briefly discusses the theory of acid-base indicators. This chapter states the contemporary state of the question. It is unfortunate that the mathematical interpretation of these theories is relegated to the next chapter by the author.

In Chapter IV "The transition interval" the author discusses the behavior of indicators in solutions quantitatively. A table is included which gives the pH intervals for color changes for a large number of indicators.

1) GOST = All-Union State Standard.

It is well known that there are a number of contradictions in the literature on this subject. It is necessary therefore to point out the literature references in separate cases, from which the respective data has been compiled; this has not been done in the book under review. All the current indicators most widely used are included in GOST 4919-49, in which pH intervals are also given. These GOST results should have been indicated, but the author does not even mention GOST. In some cases it is not clear which indicators are under discussion, because the structure is not given. E.g. in addition to the normal methyl red, other methyl reds with different pH intervals are given (p.69). The concept of pK as the pH at which 50% of the indicator is in the alkaline form and the other 50% in the acid form, should have been given on p.65 and not on p.84, since it should logically precede the table mentioned above. Fluorescent indicators are recommended (see Table on p.106) without a sufficiently critical evaluation of their properties. For β-methylumbelliferone the pH interval is given as 6-7.2, while according to Pukirev and Maslova (Factory Lab 11, 1038, 1934) max. fluorescence corresponds to a pH of 7.2-7.4. To call ultraviolet radiation "black light" (p.107) does not follow. The section on "sensitivity of indicators" has been compiled in rather an abstract manner. The sensitivity of an indicator can be defined in the same manner as for other reagents for color reactions. (see P. I. Alekseev's article, loc.cit.). The absence of a chapter on the "Testing of Indicators" is a serious omission.

In Chapter V the author considers the question of pH change during titration, but does not say anything re the fact that curves which express the relation between pH and the number of mls of added acid or alkali can be obtained either calculation or potentiometrically. In this connection the derivation of _ as somewhat nebulously expressed; at this juncture something should have been said about titration with "observers". In speaking of the increase in accuracy of titration it would have been useful to mention the application of "macro-micro burettes" (See Factory Lab.7, 627, 1938). On p.126, green is called the supplementary color to violet.

In Chapter VI colorimetric methods for the determination of pH are considered and the effect of salts, organic solvents and other materials discussed.

This chapter is well put together – the section on the mistakes which can arise in the determination of pH contains many new results. The comparator should have been mentioned in this chapter when discussing the determination of pH without buffers (p.134). This simple apparatus is described in the next chapter on p.170. In the section on universal indicators (p.139) it is completely useless to give the composition of these indicators without giving the respective amounts of each component.

For the universal indicator "MVF" (p.141) there is no indication of the pH range. It should have been pointed out that when working with universal indicators it is possible to use a color scale made on paper.

In Chapter VII "The colorimetric determination of pH in turbid and colored solutions" new data are presented. The author's own results are included for the determination of pH with organic solvents which do not mix with the solutions whose pH is being determined but which extract the indicator to different extents.

A very useful set of indicators recommended by the author for specific purposes is included. Literature relating to different sections of the book is distributed throughout the book rather unsuccessfully. There is no reference to Kolthoff and Laitinen's book "Determination of Hydrogen Ion Concentration and Electrotitration", Moscow 1947. Without dealing with smaller drawbacks in this book we should like to say that Yu. V. Karyakin's book despite a number of drawbacks is a valuable textbook for workers in Scientific-Research Laboratories.

G. A. Pevtsov

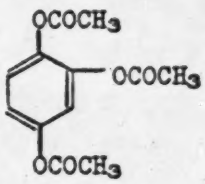
NEW REAGENTS

"PYROGALLOL A"

A chemical reagent for the determination of oxygen in gas analysis. (Catalog of chemical reagents and preparations. Bureau of Chemical Reagents, State Chemical Press, 1951, No. 1907.

A new chemical reagent for the determination of oxygen in gas analyses, "Pyrogallol A" has been proposed by the Institute of Chemical Reagents.

"Pyrogallol A" is hydroxyhydroquinone triacetate (1,2,4-trihydroxybenzene triacetate)



1 mole of "Pyrogallol A" absorbs an equal amount of oxygen, 1.5 mole, ordinary pyrogallol (1,2,3-trihydroxybenzene).

The advantage of "Pyrogallol A" as compared with ordinary pyrogallol is that on absorption of oxygen it does not evolve CO.

"Pyrogallol A" is a valuable substitute for ordin ry pyrogallol in the determination of oxygen in gas analysis.

"Pyrogallol A" is on sale at all the shops of the Bureau of Chemical Reagents. Instructions for the use of "Pyrogallol A" for the determination of oxygen in gas analysis is enclosed with each packet of reagent.